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XLI.—THE COMPOSITION OF PETROLEUM.

ON THE HYDROCARBONS IN PENNSYLVANIA PETROLEUM WITH BOILING-POINTS ABOVE 216°.

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In a former paper[1] the principal hydrocarbons in Pennsylvania, Ohio, and Canadian petroleum with boiling-points below 216°, were shown to have the composition represented by the general formula C_nH_{2n+2}. Concerning the constituents with higher boiling-points very little is known. Pelouze and Cahours[2] collected distillates to which they gave the following formulas:

216°–218°	236°–240°	255°–260°	280°
$C_{13}H_{28}$	$C_{14}H_{30}$	$C_{15}H_{32}$	$C_{16}H_{34}$

From paraffin the following hydrocarbons have been separated (Beilstein's Handbook):

212°–215°	230°–235°	252°–255°	273°–275°
$C_{13}H_{28}$	$C_{14}H_{30}$	$C_{15}H_{32}$	$C_{16}H_{34}$

[1] Proc. Am. Acad., **32**, 121.

[2] Ann. chim. phys., [4], **1**, 5 (1864).

So far as I am aware these are the only allusions to the composition of Pennsylvania petroleum in these portions. It appears that the distillations were made under ordinary atmospheric pressure in presence of air, with no attempts to avoid decomposition under these conditions.

Then, furthermore, as I have suggested in a former paper, the high specific gravity of the distillates separated by Pelouze and Cahours indicate that their distillates were obtained from Canadian petroleum. It does not appear that any attempts have been made to ascertain the molecular weights of the individual hydrocarbons. Indeed, this has been possible only within recent years, since the freezing- and boiling-point methods for the determination of molecular weights have been known. Then it is not possible to determine the vapor densities of these hydrocarbons, because, as I have recently ascertained, even *in vacuo* small quantities of the hydrocarbons such as are used in vapor density determinations undergo serious decomposition; and this occurs even in oils that have been distilled many times over in bulk *in vacuo*. In the earlier work it was evidently assumed that a few distillations under atmospheric pressure were sufficient to collect the individual hydrocarbons within the limits of their boiling-points, sufficient at least to afford reliable data as to their composition. A glance at the small differences in percentage composition is sufficient to show that it is not possible by analysis alone of products even well purified to distinguish between homologous members of a series, although such analysis may define the series.

But the chief difficulty is to obtain each hydrocarbon uncontaminated by any admixture of its homologues or by products of decomposition. This is well illustrated by the experience of Markownikoff in separating the hydrocarbons in the Russian oil, who found it impossible to collect distillates closer than limits of 5° on account of decomposition. That the same is true, perhaps in a less degree, in distillates from Pennsylvania oil is evident whenever distillation is made of the higher portions under atmospheric pressure. The rank odor is evidence of cracking. Yet the constituents with higher boiling-points are under the influence of vapor tension as much as the

constituents with lower boiling-points, and consequently require as prolonged distillation for complete or approximately complete separation. In my experience it is only possible to obtain even an approximate separation by exclusion of air and depression of boiling-points.

In this manner the higher hydrocarbons may be distilled any number of times with no appreciable decomposition. The only limit is the patience of the operator. But the stability of these hydrocarbons is evidently dependent on the influence of mass. Since, as mentioned above, while distillation of any considerable quantity of the oil may be carried on indefinitely, a limited quantity cannot be volatilized even *in vacuo* without decomposition. Many attempts to determine the vapor density of the hydrocarbons in Pennsylvania and California petroleum by volatilization *in vacuo*, according to the method of Lunge and Neuberg, have failed on account of cracking, even so far as the separation of sooty carbon from the members with high boiling-points.

In September, 1896, I set out to ascertain the composition of the principal hydrocarbons in Pennsylvania petroleum with boiling-points above 216° so far as they can be separated by distillation on a laboratory scale. Through the courtesy of the Standard Oil Company, I procured a barrel of crude oil from Oil City, and this material has been used to separate the hydrocarbons that will be described in this paper. That this oil was an approximately average specimen of Pennsylvania petroleum, appears from its properties. A determination of the specific gravity of the crude oil at 20° gave 0.8095. A combustion of the oil dried over sodium gave the following percentages of carbon and hydrogen: Carbon, 85.80; hydrogen, 14.04. Eight hundred grams distilled in the ordinary way in the following proportions:

50°–150°	150°–200°	200°–250°	250°–300°	+300°
166	88	83	100	337

Fifty-six kilograms of the crude oil were distilled in quantities of 10 liters each in a porcelain still, collecting under atmospheric pressure to 200°, and within limits of 10° under a

vacuum of 50 mm. to 300°, then within limits of 5°, and finally within limits of 2°. After eight distillations the following proportions collected :

	124°–126°	136°–138°	156°–158°	174°–176°	188°–199°
Grams,	125	145	240	205	240

199°–201°	210°–212°	226°–228°	242°–244°
225	335	150	130

Since the weights of these fractions represent all that came from the original crude oil, it is possible to gain a very general idea of the proportion of the hydrocarbons which are contained in the crude oil. But such estimation must be only approximate from the fact that any distillation, however thorough, gives only an approximate separation, and a considerable portion of any hydrocarbon must be contained in the intermediate distillates.

The percentages of the weights are as follows :

$C_{13}H_{28}$	$C_{14}H_{30}$	$C_{15}H_{32}$	$C_{16}H_{34}$	$C_{17}H_{36}$
124°–126°	136°–138°	156°–158°	174°–176°	188°–199°
0.22	0.26	0.43	0.37	0.43 per cent

$C_{18}H_{38}$	$C_{19}H_{40}$	$C_{20}H_{42}$	$C_{21}H_{44}$
199°–201°	210°–212°	230°–232°	242°–244°
0.40	0.60	0.27	0.23 per cent

In the intervals between these fractions the weights were much smaller.

After the eighth distillation each fraction was agitated at first with common concentrated sulphuric acid until the acid was not much colored, and then several times with fuming sulphuric acid. That the distillates consist almost entirely of the principal hydrocarbon is shown by the slight change in specific gravity by the acid treatment :

156°–158°	174°–176°	182°–184°	
0.805	0.8064	0.8100	Original distillate.
0.7992	0.8031	0.8093	After treatment with acid.

There was some loss in weight of the fraction by the acid treatment, but it was doubtless due, for the most part, to solution of the principal hydrocarbons in the acid. The weights of the fractions before and after treatment were as follows :

156°–158°	174°–176°	182°–186°
240	215	205
195	190	155

This solvent action has been observed in other oils with high boiling-points in continuous treatment with fuming sulphuric acid, which caused a gradual loss without changing materially the specific gravity. After the purification with the acid, distillation was continued through a Hempel column filled with glass beads or broken glass, under 50 mm. within limits of 1°, until the hydrocarbons collected in considerable quantities. After the thirtieth distillation the hydrocarbons came together within the following limits:

124°–126° 142°–143° 158°–159° 173°–174° 189°–190° 198°–199°

Even after nearly continuous distillation of sixteen months, these products showed very little indication of decomposition. Leaks in the apparatus immediately cause decomposition, as shown by a disagreeable odor, and the appearance of the distillates. So long as air is excluded from the hot vapors there is no danger of decomposition. But as we found, in attempting to ascertain the boiling-points under atmospheric pressure, a single distillation in air causes a very rank odor of decomposition.[1]

In determining the boiling-points of these hydrocarbons under atmospheric pressure, 70 grams of the fraction 124°–126° distilled as follows, under 760 mm. and with the mercury column all within the vapor:

	224°–225°	225°–226°	226°–227°	227°–228°	228°–229°
Grams, 4		28	26	3	3

Colored residue, 6

The portions between 225° and 227° collected almost entirely between 225°.5 and 226°.5.

The fraction 142°–143° nearly all distilled at 237°–238° atmospheric pressure, the fraction 158°–159° at 256° to 257°, the

[1] The difference in stability of the constituents of different petroleums is shown by their behavior when air comes in contact with the hot vapors. In accidents that have occurred during distillation, letting in air on the hot vapors, in the case of Pennsylvania petroleum the still becomes filled with dark vapors, but in a distillation of Russian petroleum, air accidentally admitted caused such a violent explosion that the thermometer was hurled across the room and broken against the wall.

raction 173°–174° at 274° to 275°, the fraction 188°–189° at 288° to 289°, and the fraction 198°–199° at 300° to 301° The hydrocarbon dodecane, $C_{12}H_{26}$, was identified in the fraction 214°–216°.[1]

Tridecane, $C_{13}H_{28}$.—The next homologue, tridecane, was sought for in the series of distillates that collected between 215° and 235°. After carrying these fractions eight times through a Hempel bead column a larger portion, 200 grams, collected at 221° to 222°. This portion was distilled twenty-four times, when 70 grams collected, as shown above. The specific gravity of the distillate before further treatment was 0.7866, and after thorough agitation with fuming sulphuric acid, 0.7834. A combustion gave the following values for carbon and hydrogen :

0.1506 gram of the oil gave 0.4690 gram CO_2 and 0.2028 gram H_2O.

	Calculated for $C_{13}H_{28}$.	Found.
C	84.78	84.94
H	15.22	14.96

The molecular weight of this oil, as determined by the Beckmann method at the freezing-point of benzene, in the hands of different workers, corresponds to that of $C_{13}H_{28}$.

I. 1.1209 grams oil and 36.3043 grams benzene gave a depression of 0°.82.

II. 1.2502 grams oil and 33.3631 grams benzene gave a depression of 1°.015.

III. 1.496 grams oil and 32.9131 grams benzene gave a depression of 1°.205.

Calculated for $C_{13}H_{28}$.	Found. I.	II.	III.
184	184.5	181	184.9

In still further confirmation of the formula of tridecane, the index of refraction was determined and its molecular refraction calculated. The index was found to be 1.4354 at 20°, and the molecular refraction as follows :

Calculated for $C_{13}H_{28}$.	Found.
61.94	61.44

[1] Proc. Am. Acad., **32**, 138.

Monochlortridecane, $C_{13}H_{27}Cl$.—In the preparation of the chlorine derivative of tridecane, chlorine was allowed to act on the hydrocarbon in screened sunlight, over water. With care to avoid an excess of chlorine, the product consisted for the most part of the monochloride. It was fractioned several times *in vacuo* under 12 mm. until considerable of the oil collected at 135° to 140°. This fraction gave as its specific gravity, at 20°, 0.8973. A determination of chlorine gave the percentage required for the monochloride:

0.1920 gram oil gave 0.1273 gram AgCl.

	Calculated for $C_{13}H_{27}Cl$.	Found.
Cl	16.23	16.39

The molecular weight as determined at the freezing-point of benzene corresponded to the same formula:

0.4585 gram oil and 18.35 grams benzene gave a depression of 0°.568.

Calculated for $C_{13}H_{27}Cl$.	Found.
218.5	216

A determination of the index of refraction confirmed the same formula; the index as determined was 1.451, corresponding to the molecular refraction:

Calculated for $C_{13}H_{27}Cl$.	Found.
65.71	66.67

Tetradecane, $C_{14}H_{30}$.—The fraction 142°–143°, collected after the twenty-fourth distillation, had the specific gravity 0.7848, after drying over sodium. After agitating with concentrated sulphuric acid, washing, and drying over sodium, it gave 0.7847. After treatment with fuming sulphuric acid it gave 0.7814. This determination, like the others, was made at 20°.

A determination of the molecular weight of this fraction, purified with fuming sulphuric acid, gave the following result:

I. 1.1049 grams oil and 36.8505 grams benzene gave a depression of 0°.735.

II. 1.052 grams oil and 35.970 grams benzene gave a depression of 0°.718.

Calculated for $C_{14}H_{30}$.	Found. I.	Found. II.
198	199.9	199.5

A combustion gave the following percentages of carbon and hydrogen :

0.1502 gram oil gave 0.4698 gram CO_2 and 0.2024 gram H_2O.

	Calculated for $C_{14}H_{30}$.	Found.
C	84.84	85.02
H	15.16	14.96

This specimen was purified with common concentrated acid; another portion purified with fuming sulphuric acid gave slightly different proportions :

0.1458 gram oil gave 0.4532 gram CO_2 and 0.1970 gram H_2O.

	Calculated for $C_{14}H_{30}$.	Found.
C	84.84	84.76
H	15.16	15.02

The boiling-point of this fraction under 760 mm. was 236° to 238°. On account of decomposition when the oil is distilled in air, it is difficult to determine the boiling-point with great precision.

A determination of the index of refraction of this hydrocarbon gave 1.4360, which corresponds to the following molecular refraction :

Calculated for $C_{14}H_{30}$.	Found.
66.54	66.36

Monochlortetradecane, $C_{14}H_{29}Cl$.—Since only small quantities of the purified hydrocarbons were available for the study of the chlorides, great care was necessary to avoid too high chlorination. Most of the hydrocarbons gave only sufficient of the chlorine derivative to verify its formula by the percentage of chlorine. The chlorine product obtained from tetradecane was fractioned *in vacuo* until it collected in larger quantities at 150°–153° under 20 mm. A determination of chlorine gave the following result :

0.1966 gram oil gave 0.1245 gram AgCl.

	Calculated for $C_{14}H_{29}Cl$.	Found.
Cl	15.25	15.65

Its specific gravity at 20° was found to be 0.9185. The quantity of product was not enough for other determinations. Another portion of the chlorine product, collected at 175° to 180°, 17 mm., gave as its specific gravity, at 20°, 1.032. A determination of chlorine gave the value required for the dichloride :

0.1937 gram oil gave 0.2125 gram AgCl.

	Calculated for $C_{14}H_{28}Cl_2$.	Found.
Cl	26.55	27.12

A determination of molecular weight at the freezing-point of benzene showed it to be the dichloride :

1.3407 grams oil and 19.81 grams benzene gave a depression of 1°.255.

Calculated for $C_{14}H_{28}Cl_2$.	Found.
267	264.3

Pentadecane, $C_{15}H_{32}$.—The specific gravity of the fraction 158°–159° (50 mm.), dried over sodium, was found to be 0.8054 at 20°. After treatment with concentrated sulphuric acid it gave 0.7939, and after thorough treatment with fuming sulphuric acid it gave 0.7896.

The molecular weight was determined by the Beckmann method :

I. 1.050 grams oil and 35.9775 grams benzene gave a depression of 0°.675.

II. 1.3946 grams oil and 23.2679 grams benzene gave a depression of 1°.37.

Calculated for $C_{15}H_{32}$.	Found.	
	I.	II.
212	211	212

Combustion I. was made of the unpurified distillate dried over sodium, and combustion II. of the oil after treatment with fuming sulphuric acid :

I. 0.1440 gram oil gave 0.4500 gram CO_2 and 0.1919 gram H_2O.

II. 0.1608 gram purified oil gave 0.5002 gram CO_2 and 0.2198 gram H_2O.

	Calculated for $C_{18}H_{32}$.	Found. I.	II.
C	84.92	85.21	84.87
H	15.08	14.80	15.20

In determining the boiling-point of pentadecane, under atmospheric pressure, it distilled almost completely at 256° to 257°.

A determination of the index of refraction gave 1.4413, from which the molecular refraction was calculated :

Calculated for $C_{15}H_{32}$.	Found.
71.15	70.49

Dichlorpentadecane, $C_{15}H_{30}Cl_2$.—With the small quantity of the hydrocarbon at hand, we did not succeed in limiting the action of chlorine to the formation of the monochloride. Fractioned *in vacuo* under 13 mm. the chlorinated product collected for the most part at 175° to 180°. This product gave as its specific gravity, at 20°, 1.0045. A Carius determination of chlorine gave the following percentage :

0.1411 gram oil gave 0.1462 gram AgCl.

	Calculated for $C_{15}H_{30}Cl_2$.	Found.
Cl	25.28	25.63

The molecular formula was established by a determination of its molecular weight :

1.4308 grams oil and 18.53 grams benzene gave a depression of 1.336.

Calculated for $C_{15}H_{30}Cl_2$.	Found.
281	283.2

Hexadecane, $C_{16}H_{34}$.—The fraction that collected at 174° to 175°, 50 mm., after the thirtieth distillation gave as its specific gravity, at 20°, 0.8000. After treatment with concentrated sulphuric acid it gave 0.7964, and after treatment with fuming sulphuric acid, 0.7911. It distilled almost completely at 275° to 276° under 760 mm. barometric pressure. In determining the molecular weight of this fraction at the freezing-point of benzene, it gave the formula $C_{16}H_{34}$:

I. 1.1507 grams oil and 35.27 grams benzene gave a depression of 0°.71.

II. 1.1833 grams oil and 35.63 grams benzene gave a depression of 0°.715.

Calculated for $C_{16}H_{34}$.	Found. I.	Found. II.
226	225.2	227.6

Determinations of carbon and hydrogen were made in the unpurified distillate (I.), in a portion purified with concentrated sulphuric acid (II.), and in a third portion purified with fuming sulphuric acid (III.), with the following results:

I. 0.1477 gram oil gave 0.4600 gram CO_2 and 0.1973 gram H_2O.

II. 0.1454 gram oil gave 0.4522 gram CO_2 and 0.1986 gram H_2O.

III. 0.1454 gram oil gave 0.4516 gram CO_2 and 0.1971 gram H_2O.

	Calculated for $C_{16}H_{34}$.	Found. I.	Found. II.	Found. III.
C	84.96	84.94	84.80	84.60
H	15.04	14.84	15.18	15.06

The index of this hydrocarbon was found to be 1.4413, from which the molecular refraction was calculated:

Calculated for $C_{16}H_{34}$.	Found.
75.750	75.555

Dichlorhexadecane, $C_{16}H_{33}Cl_2$.—The chlorine product obtained from hexadecane collected for the larger part at 205° to 210°, under 16 mm. Its specific gravity was 1.0314 at 20°. A determination of chlorine gave a value required for the dichloride:

0.1477 gram oil gave 0.1525 gram AgCl.

	Calculated for $C_{16}H_{32}Cl_2$.	Found.
Cl	24.61	24.44

This formula was also confirmed by its molecular weight:

0.5019 gram oil and 18.21 grams benzene gave a depression of 0°.457.

Calculated for $C_{18}H_{38}Cl_2$.	Found.
295	295

A portion of the original distillate 174°–175° was cooled to —10°, which caused the separation of a crystalline mass. It was filtered cold, but the solid remaining formed but a small part of the original oil.

The specific gravity of the filtered oil, 0.8005, was slightly higher than that of the unfiltered distillate. The quantity of the solid was not sufficient for analysis or further examination. No further examination was made of the filtered oil, for it was evident that the small amount of solid hydrocarbon could not change the composition nor other constants, especially since, as shown above, the original distillate has the composition of the series C_nH_{2n+2}.

Heptadecane, $C_{17}H_{36}$.—The fraction which collected at 188° to 190° after the forty-second distillation gave as its specific gravity, at 20°, after drying over sodium, 0.8017. After agitation with sulphuric acid it gave 0.8019, and after purification with fuming sulphuric acid, 0.8000. Under 760 mm. pressure this oil distilled almost entirely at 288° to 289°, with very little residue above 289°. The small residue was badly colored from decomposition. Evidently it would not be possible to distil this oil continuously under atmospheric pressure in presence of air without serious decomposition.

The formula of this distillate was established by two determinations of its molecular weight and by analysis.

I. 1.4294 grams oil and 25.7086 grams benzene gave a depression of 1°.17.

II. 1.4382 grams oil and 25.6785 grams benzene gave a depression of 1°.18.

Calculated for $C_{17}H_{36}$.	Found. I.	II.
240	241.2	240.9

Analysis I. was made of the unpurified oil dried over sodium, and analysis II. after purification with fuming sulphuric acid.

I. 0.1534 gram oil gave 0.4778 gram CO_2 and 0.2044 gram H_2O.

II. 0.1491 gram oil gave 0.4641 gram CO_2 and 0.2014 gram H_2O.

	Calculated for $C_{17}H_{36}$.	Found. I.	II.
C	84.96	84.94	84.87
H	15.04	14.80	15.01

Monochlorheptadecane, $C_{17}H_{35}Cl$.—The chlorine product from heptadecane collected in considerable quantity at 175° to 177° (15 mm.). Its specific gravity, at 20°, was found to be 0.8962. The percentage of chlorine corresponded to the monochloride:

0.1510 gram oil gave 0.0807 gram AgCl.

	Calculated for $C_{17}H_{35}Cl$.	Found.
Cl	12.92	13.21

On cooling a portion of the distillate 188°–189° to —10° it formed a pasty mass from which a small amount of a crystalline solid was obtained by filtration. The solid, after crystallization from ether and alcohol, melted at approximately 10°. The amount of solid was not sufficient for purification or examination. The filtered oil gave as its specific gravity, at 20°, 0.8035, slightly higher than that of the distillate before filtration. Since the original distillate had the composition of the series C_nH_{2n+2}, it did not seem worth while to make any further examination of the filtered oil.

Octodecane, $C_{18}H_{38}$.—After the twenty-sixth distillation larger quantities of distillates collected between 198° and 204°, mostly at 199° to 200° (50 mm.). The fraction 199°–200° distilled for the most part, although with considerable colored residue and bad odor, at 300° to 301°, under 760 mm. After drying over sodium its specific gravity was 0.8054, after agitation with sulphuric acid 0.8035, and after purification with fuming sulphuric acid 0.8017, at 20°.

Its molecular weight was ascertained by the Beckmann method at the freezing-point.

I. 0.9963 gram oil and 36.4129 grams benzene gave a depression of 0°.53.

II. 0.9926 gram oil and 23.2544 grams benzene gave a depression of 0°.84.

Calculated for $C_{18}H_{38}$.	Found. I.	II.
254	252.7	254.2

Combustion I. was made of the unpurified distillate dried over sodium; combustion II., of the oil after purification with concentrated sulphuric acid; and combustion III., after treatment with fuming sulphuric acid.

I. 0.1423 gram oil gave 0.4435 gram CO_2 and 0.1915 gram H_2O.

II. 0.1513 gram oil gave 0.4702 gram CO_2 and 0.2054 gram H_2O.

III. 0.1524 gram oil gave 0.4727 gram CO_2 and 0.2064 gram H_2O.

	Calculated for $C_{18}H_{38}$.	Found. I.	II.	III.
C	85.06	85.02	84.76	84.59
H	14.94	14.96	15.09	15.05

It is evident from the slight change in specific gravity after purification, and the percentages of carbon and hydrogen, that the original distillate consisted to a large extent of octodecane.

Monochloroctodecane, $C_{18}H_{37}Cl$.—The product obtained by the action of chlorine on octodecane collected in greater part at 185° to 190°, under 15 mm., and this fraction gave as its specific gravity, at 20°, 0.9041. The percentage of chlorine corresponded to the monochloride:

0.1482 gram oil gave 0.0782 gram AgCl.

	Calculated for $C_{18}H_{37}Cl$.	Found.
Cl	12.35	13.05

The results given above were obtained with the hydrocarbon that was liquid at ordinary temperatures. When it was found that crystals separated from this distillate at 3°, and that it became pasty at 0°, it was cooled to —10°, when it became so thick that it filtered only slowly. The solid, after filtering, was melted and again cooled and filtered, after which it was perfectly white. It was then crystallized from ether and alcohol, after which it melted at 20°. It was estimated that 20 per cent of the original oil separated as the solid hy-

drocarbon on cooling. It was difficult to separate the solid completely on account of the great solvent action of the oil.

The filtered and pressed solid melted at 20°, and after crystallization from ether and alcohol and from gasoline, the melting-point could not be raised. Krafft[1] gave 28° as the melting-point of octodecane which he obtained from stearic acid, but his octodecane boiled at 214°.5 under 50 mm. pressure. The specific gravity of the solid hydrocarbon was 0.7830 at $\frac{20°}{20°}$, and 0.7816 at $\frac{20°}{4°}$. Krafft gave 0.7768 as the specific gravity of $C_{18}H_{38}$ at 28°. A determination of the molecular weight of the purified hydrocarbon confirmed its formula :

1.1003 grams oil and 19.65 grams benzene gave a depression of 0°.941.

Calculated for $C_{18}H_{37}Cl$.	Found.
288.5	291.5

This molecular weight, showing that the hydrocarbon boiling at 300° is octodecane, does not agree with Krafft's conclusion as to the formula of the hydrocarbon obtained from stearic acid. In heating stearic acid with hydriodic acid Krafft assumed that all the oxygen is removed, leaving intact the carbon of the carboxyl, with the formation of octodecane. But when this work was done the only means of verifying the formula was by analysis, which was sufficient to determine the series, but not the individual members of the series. While the results of Krafft's combustions gave almost exact values for the formula $C_{18}H_{38}$, the size of the molecule could not be determined. Krafft looked upon the hydrocarbon boiling at 303° as having the formula $C_{17}H_{36}$.

The specific gravity of the oil, after cooling and filtration, was somewhat higher than before, 0.8110 at 20°, and higher than the specific gravity of the filtered solid octodecane, 0.7830. The molecular weight of the filtered oil was the same as before filtration.

0.9904 gram substance and 16.10 grams benzene gave a depression of 1°.184.

Calculated for $C_{18}H_{38}$.	Found.
254	254.6

[1] Ber. d. chem. Ges., 15, 1703 (1882).

A combustion of the liquid hydrocarbon showed some change in the proportion of carbon and hydrogen :

0.1483 gram substance gave 0.4636 gram CO_2 and 0.1954 gram H_2O.

	Calculated for $C_{18}H_{38}$.	$C_{18}H_{36}$.	Found.
C	85.70	85.06	85.25
H	14.30	14.94	14.64

While there is a narrow difference in calculated percentages between the two formulæ, the percentages found, together with the higher specific gravity, indicate that the filtered oil was a mixture of the two series C_nH_{2n} and H_nC_{2n+2}.

A determination of the index of refraction, which was found to be 1.4435, and the molecular refraction correspond more nearly to the formula $C_{18}H_{36}$:

Calculated for $C_{18}H_{38}$.	$C_{18}H_{36}$.	Found.
82.90	84.96	82.60

A combustion of the solid hydrocarbon gave proportions required for the series C_nH_{2n+2} :

0.1564 gram substance gave 0.4883 gram CO_2 and 0.2083 gram H_2O.

	Calculated for $C_{18}H_{38}$.	Found.
C	85.06	85.15
H	14.94	14.80

The position in the series was shown by its molecular weight :

I. 1.9475 grams of the solid and 25.21 grams benzene gave a rise of 0°.7734.

II. 1.9475 grams of the solid and 25.28 grams benzene gave a rise of 0°.7830.

Calculated for $C_{18}H_{38}$.	Found. I.	II.
254	256	253.2

The formula of octodecane was further confirmed by its index of refraction. The index was found to be, at 20°, 1.440, which corresponds to the molecular refraction :

Calculated for $C_{18}H_{38}$.	Found.
84.96	84.53

Nonodecane, $C_{19}H_{40}$.—In the eighth distillation, under 50 mm., 335 grams collected at 210° to 212° with much smaller weights on either side. After continuing the distillation twenty-seven times, a portion of the fraction 210°–212° was purified with fuming sulphuric acid; before this treatment the oil gave as its specific gravity, at 20°, 0.8274, and afterward, 0.8122. In determining its molecular weight by the freezing-point method the following values were obtained:

I. 1.1039 grams oil and 39.7462 grams benzene gave a depression of 0°.575.

II. 1.1418 grams oil and 36.2175 grams benzene gave a depression of 0°.505.

Calculated for $C_{19}H_{40}$.	Found. I.	Found. II.
268	269.5	268

Determinations of carbon and hydrogen gave values for the series C_nH_{2n+2}:

I. 0.1530 gram oil gave 0.4771 gram CO_2 and 0.1994 gram H_2O.

II. 0.1591 gram oil gave 0.4976 gram CO_2 and 0.2132 gram H_2O.

	Calculated for $C_{19}H_{38}$.	Calculated for $C_{19}H_{40}$.	Found. I.	Found. II.
C	85.70	85.08	85.04	85.29
H	14.30	14.92	14.48	14.89

Analysis I. was made of the oil before purification, and analysis II. afterward.

A determination of the index of refraction gave 1.4522, which corresponds to the following molecular refraction:

Calculated for $C_{19}H_{40}$.	Found.
89.55	88.68

The results on the composition of the distillate 210°–212° were obtained on the purified distillate without cooling to separate the solid hydrocarbon. On cooling a portion of this distillate to —10°, filtering cold and pressing the solid, 5 grams of the solid hydrocarbon and 30 grams of the liquid hydrocarbon were obtained; the solid hydrocarbon, therefore, formed a small part of the original distillate. The specific gravity of

the filtered oil was 0.8208 at 20°. The specific gravity of the distillate before cooling, as shown above, was 0.8122 at 20°.

After crystallization from ether and alcohol, the specific gravity of the solid hydrocarbon was 0.7725 at $\frac{20°}{4°}$ and 0.7781 at $\frac{20°}{4°}$.

A determination of its molecular weight gave a value required for the hydrocarbon $C_{19}H_{40}$.

1.4011 grams of the solid and 26.66 grams benzene gave a rise of 0°.496.

Calculated for $C_{19}H_{40}$.	Found.
268	271.6

The melting-point of the solid was found to be 33° to 34°, corresponding to the melting-point, 32°, that Krafft found for the solid hydrocarbon distilling at 226°.5, 50 mm.

A combustion of the oil filtered from the solid hydrocarbon gave percentages of carbon and hydrogen required for $C_{19}H_{38}$:

0.1495 gram oil gave 0.4715 gram CO_2 and 0.1928 gram H_2O.

Calculated for $C_{19}H_{38}$.	Found.
85.70	86.00
14.30	14.33

A determination of the molecular weight confirmed the formula.

2.5445 grams oil and 24.63 grams benzene gave a rise of 0°.994.

Calculated for $C_{19}H_{38}$.	Found.
266	267

The formula was further verified by its index of refraction. It gave the index 1.4515, corresponding to the molecular refraction:

Calculated for $C_{19}H_{38}$.	Found.
87.46	87.51

With the distillate 212°–214°, 50 mm., the limit is reached of the solid hydrocarbons whose molecular weight can be determined by the freezing-point method on account of the crys-

tallization of the hydrocarbon before the benzene freezes. The molecular weights of solid higher members were determined by the boiling-point method.

The results described in this paper defining the physical properties and formulas of the hydrocarbons separated from Pennsylvania petroleum differ in several essential particulars both from the hydrocarbons obtained by Krafft by decomposition of the monobasic acids with high molecular weights, and those formerly reported as among the constituents of Pennsylvania oil. It has been shown that the hydrocarbon which boils at 196° is undecane, $C_{11}H_{24}$, and not dodecane as found by Pelouze and Cahours. Likewise, the hydrocarbon which boils at 216° proved to be dodecane and not tridecane. Since there was no method for ascertaining the molecular weights of these bodies at the time when they were separated by Pelouze and Cahours, and elementary analysis could only determine the series, it was only by analogy that the homologous members of the series could be guessed at. Since 182° was accepted as the boiling-point of undecane, naturally dodecane and tridecane should fall into the fractions which boil at 196° and 216°.

The boiling-point of tridecane has been variously stated at 219°, 216°, and 212° to 215°. But neither of these temperatures can be accepted as the boiling-points of tridecane since its molecular weight is found to be that of the hydrocarbon boiling at 225° to 226°.

The hydrocarbon tetradecane boils at 236° to 238°, the same boiling-point as was assigned to the tridecane separated by Pelouze and Cahours, but the specific gravity of tetradecane, 0.7812 at 20°, is essentially lower than that found by Pelouze and Cahours, 0.809.

Pentadecane, boiling-point 156° to 157°, is nearly the same in boiling-point as the hydrocarbon separated by Pelouze and Cahours, boiling-point 260°, although its specific gravity, 0.7896 at 20°, is much lower than they found, —0.825 at 19°.

The boiling-point of hexadecane is not very different from that given by Pelouze and Cahours, but its specific gravity is considerably lower. It does not differ materially in boiling-

point from hexadecane, which Krafft obtained by heating palmitic acid, nor from that of hexadecane, boiling-point 278°, obtained by Zincke from normal octyl iodide.[1] Since, however, the oils obtained by freezing out the solid hydrocarbons have specific gravities considerably higher than those of the original distillates, and apparently belong to another series, as shown by analysis and refraction indices, it is possible that the solid hydrocarbons held in solution in the oils have their boiling-points depressed in the fractional distillation by which they were separated from the main body of the crude oil. Still, the molecular weights of the solid hydrocarbons correspond to definite formulas; for instance, from the distillate 300°–301°, atmospheric pressure, octodecane was separated in a practically pure form.

The less volatile portions of Pennsylvania petroleum consist of several series of hydrocarbons. The series C_nH_{2n} is liquid even at low temperatures, of higher specific gravity, and another is composed of solid hydrocarbons of the series C_nH_{2n+2}.

In a former paper[2] it was shown that the high values assigned by Pelouze and Cahours as the specific gravity of the distillates separated by them from petroleum, indicated that their hydrocarbons were separated from Canadian petroleum. The same inference is supported by the high specific gravity of the hydrocarbons boiling above 216°, which were separated by Pelouze and Cahours, as compared with the specific gravity of the hydrocarbons, separated from Pennsylvania petroleum, described in this paper.

After establishing a homologous series by analysis, evidently the only means available for Pelouze and Cahours to determine the molecular size of the hydrocarbons was to assume that a hydrocarbon constituted the chief portion of any distillates that collected in unusually large amounts, and to compute the series in unbroken order from the lower members.

Several attempts were made to show the presence of the hydrocarbon $C_{20}H_{42}$, but the distillates between the limits 215°

[1] Ann. Chem. (Liebig), 182, 15.
[2] Proc. Am. Acad., 32, 171.

and 225° were small, and in none of them did the molecular weight obtained correspond to this formula.

Heneicosane, $C_{21}H_{44}$, *and Liquid Hydrocarbon*, $C_{21}H_{42}$. *From Distillate 230°–232°, 50 mm.*—Larger quantities of distillates amounting to 200 grams collected at 230° to 232°, for the most part at 230° to 231°. The specific gravity of the unpurified distillate was 0.8321; after purification it gave 0.8230. A combustion of the purified oil gave the following percentages of carbon and hydrogen:

0.1540 gram oil gave 0.4813 gram CO_2 and 0.1968 gram H_2O.

	Calculated for C_nH_{2n}.	Calculated for $C_{21}H_{44}$.	Found.
C	85.70	85.14	85.23
H	14.30	14.86	14.32

There was evidently some loss in this analysis, but the percentages are more satisfactory for the formula $C_{21}H_{42}$. It will be shown that this distillate was a mixture of a solid hydrocarbon with an oil of higher specific gravity. Its molecular weight was determined at the freezing-point of benzene.

I. 1.4807 grams oil and 25.9125 grams benzene gave a depression of 0°.949.

II. 0.6845 gram oil and 19.48 grams benzene gave a depression of 0°.579.

Calculated for $C_{21}H_{42}$.	Calculated for $C_{21}H_{44}$.	Found. I.	Found. II.
294	296	295	297.4

The index of refraction of this hydrocarbon was found to be 1.4608, corresponding to the molecular refraction:

Calculated for $C_{21}H_{42}$.	Found.
96.66	96.91

The molecular weight and molecular refraction show that this distillate is composed of a hydrocarbon containing 21 carbon atoms, and the combustion and the high specific gravity point to the series C_nH_{2n}.

A portion of the oil was cooled to —10°, filtered cold, the solid well pressed in filter-paper, and crystallized from ether and alcohol. The ready solubility of these solid hydrocar-

bons in ether and their insolubility in alcohol afford an easy means of purification. The melting-point of the purified solid was 40° to 41°.

A combustion gave the following values for carbon and hydrogen:

0.1353 gram substance gave 0.4237 gram CO_2 and 0.1778 gram H_2O.

	Calculated for $C_{21}H_{44}$.	Found.
C	85.13	85.39
H	14.87	14.72

The filtered oil gave as its specific gravity, at 20°, 0.8424. The percentages of carbon and hydrogen were ascertained by a combustion:

0.1498 gram oil gave 0.4724 gram CO_2 and 0.1898 gram H_2O.

	Calculated for $C_{21}H_{42}$.	Found.
C	85.70	85.98
H	14.30	14.08

Its molecular weight was determined at the freezing-point of benzene.

0.9466 gram oil and 21.01 grams benzene gave a depression of 0°.737.

Calculated for $C_{21}H_{42}$.	Found.
294	299

Docosane, $C_{22}H_{46}$, *and Liquid Hydrocarbon*, $C_{22}H_{44}$. *From Distillate 240°–242°, 50 mm.*—After the thirtieth distillation 150 grams collected at 240° to 242°, which gave as its specific gravity, before purification, 0.8341. After purification with fuming sulphuric acid its specific gravity was 0.8262. Combustions gave the following percentages of carbon and hydrogen:

I. 0.1538 gram oil gave 0.4800 gram CO_2 and 0.1992 gram H_2O.

II. 0.1560 gram oil gave 0.4874 gram CO_2 and 0.2024 gram H_2O.

III. 0.1362 gram oil gave 0.4257 gram CO_2 and 0.1788 gram H_2O.

	Calculated for $C_{22}H_{44}$.	Calculated for $C_{23}H_{46}$.	Found. I.	Found. II.	Found. III.
C	85.70	85.16	85.09	85.21	85.25
H	14.30	14.84	14.40	14.42	14.59

The molecular weight was determined as follows:

I. 0.8367 gram oil and 20.38 grams benzene gave a depression of 0°.642.

II. 2.5442 grams oil and 21.91 grams benzene gave a rise in boiling-point of 0°.9566.

Calculated for $C_{22}H_{44}$.	Found. I.	Found. II.
308	313.4	311.3

The index of refraction was found to be 1.454 and the molecular refraction:

Calculated for $C_{22}H_{44}$.	Found.
101.27	100.7

The distillates in the vicinity of 240°, 50 mm., deposited no solid on standing at ordinary temperatures, but higher fractions all deposited solids. When cooled to 0°, the fraction 242°–254° became nearly solid. After further cooling to —10° the solid was filtered in a funnel surrounded with salt and ice, pressed in filter-paper, and crystallized from ether and alcohol. The solid melted at 43°, and when further purified from gasoline, at 44°. Kraft gave 44°.4 as the melting-point of the hydrocarbon $C_{22}H_{46}$. Its specific gravity at 60° was found to be 0.7796. A combustion gave proportions of carbon and hydrogen required for the series C_nH_{2n+2}.

0.1521 gram of the solid gave 0.4721 gram CO_2 and 0.2021 gram H_2O.

	Calculated for $C_{22}H_{44}$.	Calculated for $C_{23}H_{46}$.	Found.
C	85.70	85.16	85.13
H	14.30	14.84	14.86

The quantity of the hydrocarbon was not sufficient for a determination of its molecular weight.

The filtered oil gave as its specific gravity, at 20°, 0.8296, a value somewhat higher than that obtained before filtration. A combustion gave the following percentages of carbon and hydrogen:

0.1505 gram oil gave 0.4717 gram CO_2 and 0.1937 gram H_2O.

0.1411 gram oil gave 0.4419 gram CO_2 and 0.1819 gram H_2O.

	Calculated for $C_{22}H_{44}$.	I.	II.
C	85.70	85.49	85.41
H	14.30	14.31	14.32

These proportions correspond to the formula $C_{22}H_{44}$, which is supported by the high specific gravity.

The molecular weight of the filtered oil was also determined:

1.0713 grams oil and 19.60 grams benzene gave a depression of 0°.858.

Calculated for $C_{22}H_{44}$.	Found.
308	312

The wide difference in specific gravity between the solid and liquid hydrocarbons which boil at 240° to 242, 50 mm., points to different series. While the percentages of carbon and hydrogen given by analysis could not alone be depended on to prove the different series, the results of combustion with specific gravity are sufficient. The differences in theoretical composition of the two series are 0.5 per cent for carbon and for hydrogen. In combustions conducted under the most favorable conditions and with the greatest care, the different series may be shown in well purified materials. But with so many determinations, and the extreme care in details of the method, while the percentages obtained are sufficiently close to indicate the series, the results are not in all cases as close to the calculated percentages as should be reached in the greater precision of a few analyses.

Tricosane, $C_{23}H_{48}$, *and Liquid Hydrocarbon*, $C_{23}H_{46}$. *From Distillate 258°–260°, 50 mm.*—After the nineteenth distillation, 175 grams collected at 258° to 260°, 50 mm., for the most part at 260° to 261° which deposited a considerable quantity of solid hydrocarbon on standing. The specific gravity of the unpurified distillate decanted from the solid was as follows:

60°, 0.8341; 70°, 0.8320; 80°, 0.8310.

The oil was agitated several times with concentrated sulphuric acid until the acid was not much colored, and washed with sodium hydroxide and water, and finally with salt brine. On account of the high specific gravity of the oil some heavy solution such as brine or calcium chloride was necessary to separate the water and oil. The oil was dried for examination over calcium chloride and metallic sodium.

The combustion of the oil gave the following percentages of carbon and hydrogen :

0.1508 gram oil gave 0.4711 gram CO_2 and 0.1945 gram H_2O.

	Calculated for $C_{23}H_{46}$.	Calculated for $C_{25}H_{48}$.	Found.
C	85.70	85.18	85.21
H	14.30	14.82	14.33

A part of the carbon dioxide was evidently lost, but the results point to the series C_nH_{2n}, which represents the composition of the oil, much the larger part of the distillate.

A portion of the distillate was cooled to —10°, and filtered cold to separate the crystalline solid. The solubility of the solid hydrocarbon seemed to diminish rapidly with lower temperatures, consequently a small proportion of the solid remains in the oil below —10°. After pressing and crystallizing from ether and alcohol, the solid melted at 45°. Krafft's hydrocarbon, $C_{23}H_{48}$, melted at 47°.7. Two determinations of its specific gravity, at 60°, gave (1) 0.7894, (2) 0.7900.

A combustion of the solid gave results for the series C_nH_{2n+2}.

0.1515 gram substance gave 0.4710 gram CO_2 and 0.1989 gram H_2O.

	Calculated for $C_{23}H_{48}$.	Found.
C	85.20	85.06
H	14.80	14.64

A determination of its molecular weight at the boiling-point of benzene was made :

1.1208 grams of the substance and 23.08 grams benzene gave a rise of 0°.412.

Calculated for $C_{23}H_{48}$.	Found.
324	327

The filtered oil gave as its specific gravity, at 20°, 0.8569. It gave percentages of carbon and hydrogen required for the series C_nH_{2n} :

0.1504 gram oil gave 0.4711 gram CO_2 and 0.1945 gram H_2O.

	Calculated for $C_{23}H_{46}$.	Calculated for $C_{23}H_{48}$.	Found.
C	85.70	85.18	85.41
H	14.30	14.82	14.36

The molecular weight was determined at the freezing-point of benzene :

3.464 grams oil and 26.06 grams benzene gave a depression of 1°.0475.

Calculated for $C_{23}H_{46}$.	Found.
322	325

The index of refraction was found to be 1.4714, from which was calculated the molecular refraction :

Calculated for $C_{23}H_{46}$.	Found.
105.87	105.31

Tetracosane, $C_{24}H_{50}$, *and Liquid Hydrocarbon*, $C_{24}H_{48}$. *From Distillate 272°–274°, 50 mm.*—After the nineteenth distillation, 150 grams collected at 272° to 274°, 50 mm., that became partly solid on standing. The decanted oil gave as its specific gravity 0.8448, at 20°. A part of the distillate was then cooled to —10°, and the solid filtered cold under pressure.

The distillate was purified by treatment with successive portions of fuming sulphuric acid until the acid was nearly colorless, then washed with sodium hydroxide and a concentrated solution of calcium chloride, and dried over fused calcium chloride and sodium. Nearly one-third of the volume was removed in purification. The purified oil then gave as its specific gravity, at 20°, 0.8598, and at higher temperatures :

60°, 0.8375 ; 70°, 0.8366 ; 80°, 0.8354.

A combustion of the purified oil gave percentages of carbon and hydrogen required for the series C_nH_{2n}.

0.1539 gram oil gave 0.4769 gram CO_2 and 0.2000 gram H_2O.

	Calculated for $C_{24}H_{48}$.	$C_{24}H_{50}$.	Found.
C	85.70	85.21	85.35
H	14.30	14.79	14.54

These percentages evidently support the formula $C_{24}H_{48}$.

A determination of the molecular weight of the liquid hydrocarbon gave at the boiling-point of benzene a result required for $C_{24}H_{48}$.

2.0681 grams oil and 25.78 grams benzene gave a rise of 0°.6096.

Calculated for $C_{24}H_{48}$.	Found.
336	337.4

The index of refraction of the oil was found to be 1.4726, from which the following molecular refraction was calculated:

Calculated for $C_{24}H_{48}$.	Found.
110.47	109.75

Specific gravity of the oil at $\frac{20°}{4°}$, 0.8582.

The solid separated by filtration melted at 48°. Krafft's hydrocarbon, $C_{24}H_{48}$, melted at 51°. It gave as its specific gravity the following values:

60°, 0.7902; 70°, 0.7893; 80°, 0.7875.

Compared with water at 4°, these results reduce to 0.7742. The specific gravity given by Krafft to tetracosane, at 4°, was 0.7784, the same as that of the solid hydrocarbon which he separated from shale oil. The solid products from Pennsylvania oil show only slight variations in specific gravity. But the heavy oils show a decided increase in specific gravity with increase in molecular weight.

A combustion gave percentages of carbon and hydrogen required for the series C_nH_{2n+2}.

0.1433 gram of the solid gave 0.4479 gram CO_2 and 0.1895 gram H_2O.

	Calculated for C_nH_{2n}.	Calculated for $C_{34}H_{50}$.	Found.
C	85.70	85.23	85.25
H	14.30	14.77	14.70

The molecular weight was determined at the boiling-point of benzene.

Calculated for $C_{34}H_{50}$.	Found.
338	337

To ascertain whether the solid which separated at ordinary temperatures was identical with what remains in solution, a portion of the oil was cooled to 0°, filtered at the same temperature, and the filtrate cooled to —10° and filtered under pressure at the same temperature. The three solids were carefully purified by crystallization from ether and alcohol, and their melting-points taken. The solid separated at ordinary temperatures melted at 48°, that separated at 6° melted at 51° to 52°, and that separated at —10° melted at 51° to 52°.

It is therefore evident that this distillate consists chiefly of one solid hydrocarbon, $C_{34}H_{50}$, and that the oil remaining liquid at —10° belongs to a different series.

Pentacosane, $C_{25}H_{52}$, *and Liquid Hydrocarbon*, $C_{26}H_{52}$. *From Distillate 280°–282°, 50 mm.*—After the fifteenth distillation, 100 grams collected at 280° to 282°, 50 mm., which deposited a larger quantity of solid hydrocarbon than the lower distillates. This solid was separated from the oil and the latter was then cooled to 0° and filtered at the same temperature.

The specific gravity of the filtered oil at 20° was 0.8580.

A combustion gave the following values:

0.1593 gram oil gave 0.4997 gram CO_2 and 0.2107 gram H_2O.

	Calculated for $C_{26}H_{52}$.	Found.
C	85.70	85.55
H	14.30	14.67

The formula was established by its molecular weight, determined at the boiling-point of benzene.

3.9867 grams oil and 30.19 grams benzene gave a rise of 0°.936.

Calculated for $C_{26}H_{52}$.	Found.
364	362

A determination of the index of refraction gave 1.4725, which corresponded to the molecular refraction :

Calculated for $C_{26}H_{52}$.	Found.
119.87	119.12

After crystallization from ether and alcohol, from which it separated in crystalline plates, the solid hydrocarbon gave percentages of carbon and hydrogen required for the series C_nH_{2n+2}.

0.1534 gram substance gave 0.4787 gram CO_2 and 0.2006 gram H_2O.

	Calculated for $C_{26}H_{52}$.	Found.
C	85.25	85.09
H	14.75	14.53

A determination of its molecular weight verified the formula.

1.7583 grams substance and 24.39 grams benzene gave, by the boiling-point method, a rise of 0°.5231.

Calculated for $C_{26}H_{52}$.	Found.
352	353.4

Melting-point of the solid hydrocarbon, 53° to 54°.

Hexacosane, $C_{26}H_{54}$, *and Liquid Hydrocarbon*, $C_{27}H_{56}$. *From Distillate 292°–294°, 50 mm.*—After the fifteenth distillation, 100 grams collected at 292° to 294°, 50 mm., which deposited a considerable quantity of solid crystalline hydrocarbon. These crystals were filtered, pressed, and purified by crystallization from ether and alcohol. Melting-point, 58°. The specific gravity of this hydrocarbon was determined as follows :

60°, 0.7977 ; 70°, 0.7956 ; 80°, 0.7943.

A combustion of the solid gave the following percentages of carbon and hydrogen :

0.1508 gram substance gave 0.4709 gram CO_2 and 0.2033 gram H_2O.

	Calculated for $C_{26}H_{54}$.	Found.
C	85.24	85.17
H	14.76	14.98

The molecular weight was ascertained at the boiling-point of benzene.

1.2754 grams substance and 24.2827 grams benzene gave a rise of 0°.416.

Calculated for $C_{26}H_{54}$.	Found.
366	364

On cooling the original distillate to —10°, it formed a thick, pasty mass. It was filtered under pressure, keeping cold. The filtered crystals were pressed and crystallized from ether and alcohol. Melting-point, 58°. The solids pressed out from the fractions from 288° to 302°, 50 mm., showed very slight variations in melting-points.

288°–290°, 56°.	300°–304°, 59°–60°.
294°–296°, 58°.	302°–304°, 59°–60°.

The oil filtered under pressure was very thick and viscous. Its specific gravity, at 26°, was 0.8688. A combustion gave the following percentages of carbon and hydrogen :

0.1500 gram oil gave 0.4750 gram CO_2 and 0.1812 gram H_2O.

	Calculated for $C_{27}H_{52}$.	Found.
C	86.17	86.36
H	13.83	13.43

The molecular weight at the boiling-point of benzene corresponded to the formula $C_{27}H_{52}$.

3.6506 grams oil and 25.80 grams benzene gave a rise of 0°.964.

Calculated for $C_{27}H_{52}$.	Found.
376	376.2

The index of refraction corresponded to the same formula.

The index was found to be 1.4722, and the molecular refraction :

Calculated for $C_{17}H_{38}$.	Found.
122	121.4

Octocosane, $C_{28}H_{58}$, *and Liquid Hydrocarbon*, $C_{28}H_{54}$. *From Distillate 310°–312°, 50 mm.*—After the tenth distillation 75 grams collected at 310° to 312°, from which a considerable quantity of crystals collected above the oil on standing. The oil separated from the crystals was then cooled to —10° and filtered cold under pressure. The solid was pressed and purified by crystallization from ether and alcohol. Melting-point, 60°. Its specific gravity was determined as follows:

70°, 0.7945; 80°, 0.7927; 90°, 0.7911.

A combustion gave the following percentages of carbon and hydrogen:

0.1508 gram substance gave 0.4703 gram CO_2 and 0.2032 gram H_2O.

	Calculated for $C_{28}H_{58}$.	Found.
C	85.28	85.07
H	14.72	14.97

The molecular weight at the boiling-point of benzene corresponded to the formula $C_{28}H_{58}$.

3.070 grams solid hydrocarbon and 26.21 grams benzene gave a rise of 0°.7538.

Calculated for $C_{28}H_{58}$.	Found.
394	399

A very thick oil, separated by filtration, gave as its specific gravity, at 20°, 0.8694. A combustion gave percentages of carbon and hydrogen required for the series C_nH_{2n-2}.

0.1500 gram oil gave 0.4729 gram CO_2 and 0.1836 gram H_2O.

	$C_{28}H_{58}$.	Calculated for $C_{28}H_{56}$.	$C_{28}H_{54}$.	Found.
C	85.28	85.70	86.02	85.96
H	14.72	14.30	13.98	13.60

The molecular weight was found at the boiling-point of benzene.

I. 2.6792 grams oil and 29.85 grams benzene gave a rise of 0°.5826.

II. 1.9196 grams oil and 27.98 grams benzene gave a rise of 0°.4459.

Calculated for $C_{28}H_{54}$.	Found. I.	Found. II.
392	396	394.4

The index of refraction was found to be 1.480, which corresponds to the molecular refractions :

Calculated for $C_{28}H_{54}$.	Found.
127	126.78

It will be observed that the two liquid hydrocarbons last described have been shown to belong to a series C_nH_{2n-2}. Results already obtained, but not yet published, indicate that the same series of hydrocarbons constitute the less volatile portions of Canadian petroleum, and probably also of Ohio petroleum. Results already published show that the less volatile distillates from California and Texas petroleum are composed of the same series and other series still poorer in hydrogen.

The unexpected appearance of the series C_nH_{2n-2} in Pennsylvania petroleum suggests a closer relationship between this petroleum and the heavier oils from other fields, such as those in Texas and California, than was suspected. To gain further information concerning the heavier portions of Pennsylvania oil, we allowed 3 kilograms of the sample from which the hydrocarbons described in this paper were prepared, to evaporate spontaneously in the air in a strong draught, but with no application of heat. At the end of thirty days there remained 1 kilogram that gave as its specific gravity 0.8620, practically the same as that of $C_{28}H_{54}$, 0.8694. A combustion gave percentages of carbon and hydrogen required for the series C_nH_{2n-2}. A distillation showed that 65 per cent of the residual oil was composed of hydrocarbons above $C_{18}H_{30}$. The composition of these hydrocarbons will be ascertained in connection with the study of natural and commercial paraffin, which is now in progress.

This interesting relation, and others between the numerous petroleums from different oil fields that have been examined in this laboratory, will be presented more at length in a later paper.

As a general summary of the results described in this paper, hydrocarbons have been identified as shown in the following table.

It appears that the liquid hydrocarbon, $C_{28}H_{54}$, in fraction 310°–312°, has the same number of carbon atoms as the solid hydrocarbon octosane in the same fraction. In this respect the hydrocarbons in this fraction differ from those in the two preceding fractions, in each of which the liquid hydrocarbon has one more carbon atom than the solid constituent. Determinations of the molecular weights of hydrocarbons with high carbon content can only be made by the boiling-point method; and even with the greatest care in manipulation this method is somewhat uncertain for high molecular weights of solid hydrocarbons, for the reason that the rise in boiling-points diminishes with the increase in molecular weight. With oils there is less difficulty. For instance, the molecular weight, 376.2, of the liquid hydrocarbon $C_{27}H_{59}$, given on page 194, is one of five closely concordant determinations by different persons. As an illustration of the care necessary in details, heating with a lamp supplied with gas from the laboratory mains is so irregular on account of variation in gas pressure that the gas must be supplied from a tank under water pressure.

Name.	Symbol.	Boiling-point.		Melting-point.
Tridecane	$C_{13}H_{28}$	226°		
Tetradecane	$C_{14}H_{30}$	236°–238°		
Pentadecane	$C_{15}H_{32}$	256°–257°		
Hexadecane	$C_{16}H_{34}$	274°–275°		
Heptadecane	$C_{17}H_{36}$	288°–289°		10°
Octodecane	$C_{18}H_{38}$	300°–301°		20°
Nonodecane	$C_{19}H_{40}$	210°–212°,	50 mm.	33°–34°
Heneicosane	$C_{21}H_{44}$	230°–231°	"	40°–41°
Hydrocarbon, liquid at −10°	$C_{22}H_{44}$	240°–242°	"	
Docosane	$C_{22}H_{46}$			44°
Hydrocarbon, liquid at −10°	$C_{23}H_{46}$	258°–260°	"	
Tricosane	$C_{23}H_{48}$			45°
Hydrocarbon, liquid at −10°	$C_{24}H_{48}$	272°–274°	"	

Name.	Symbol.	Boiling-point.	Melting-point.
Tetracosane	$C_{24}H_{50}$		48°
Hydrocarbon, liquid at −10°	$C_{26}H_{52}$	280°–282° 50 mm.	
Pentacosane	$C_{25}H_{52}$		53°–54°
Hydrocarbon, liquid at −10°	$C_{27}H_{52}$	292°–294° "	
Hexacosane	$C_{26}H_{54}$		58°
Hydrocarbon, liquid at −10°	$C_{28}H_{54}$	310°–312° "	
Octocosane	$C_{28}H_{58}$		60°

Much attention has been given to these determinations, especially by Messrs. O. J. Sieplein and R. P. Cushing.

The preparation of the distillates described in this paper was begun December 1, 1896, by Mr. A. S. Kittelberger, who distilled 56 kilograms of Pennsylvania crude oil. The distillations were later continued by different assistants. The following gentlemen have also aided in the purification, examination, and analysis of these hydrocarbons: Messrs. Shaw, Latimer, R. P. Cushing, Dr. E. J. Hudson, and O. J. Sieplein. To the latter especially is due the analysis and identification of the chlorine derivatives of the hydrocarbons.

Contributions from the Kent Chemical Laboratory of the University of Chicago.

ON SOME HYDROXYLAMINE COMPOUNDS.[1]

By Maxwell Adams.

As a reagent in organic chemistry hydroxylamine has been carefully investigated, but from the standpoint of inorganic chemistry it has not received much attention, and the investigations in this field are in many places incomplete or contradictory. One reason for this neglect has been the cost and trouble of preparing it by the ordinary methods. These difficulties have now been overcome by the very economical and satisfactory method of Divers and Haga.[2]

The results obtained by Hofmann,[3] Rammelsberg,[4] and Pesci,[5] on the mercuramines, indicate a parallel line of work

[1] The author's inaugural dissertation submitted to the faculties of the Graduate Schools of Arts, Literature, and Science of the University of Chicago, in candidacy for the degree of Doctor of Philosophy.

[2] J. Chem. Soc. (London), **69**, 1665.

[3] Ann. Chem. (Liebig), **308**, 191.

[4] J. prakt. Chem., **38**, 558.

[5] Ztschr. anorg. Chem., **21**, 361.

with hydroxylamine because of its relationship to ammonia.

The similarity of hydroxylamine to both water and ammonia indicates that through a study of it as a solvent some light might be thrown upon the part played by these liquids in crystallization. Pure hydroxylamine is a liquid above 33°; it might be used as a solvent in determining the electrolytic conductivity of solutions, and it would be interesting to note if it resembles water or ammonia in this particular.

The consideration of these facts, among others, led Dr. Lengfeld to suggest to me a study of hydroxylamine as a promising field for work. A review of the methods of preparation and estimation of hydroxylamine, its action on salts of mercury, and the properties of some of its halogen salts which have been hitherto overlooked, are considered in this article.

When the study was begun many conflicting statements were found, and it at once became evident that much work needed repetition, and a not inconsiderable part of this paper is devoted to a review of previous work. Attention was first directed towards the methods ordinarily used in the estimation of hydroxylamine; these were found inaccurate, and before any progress in this work could be made they had to be revised. Volumetric methods for the determination of hydroxylamine were first carried out in a systematic manner by Meyeringh,[1] who recommended three different processes:

1. The reduction of ferric sulphate with hydroxylamine and estimation of the ferrous sulphate with potassium permanganate.

2. The reduction of Fehling's solution.

3. The titration with free iodine solution in the presence of sodium phosphate or sodium bicarbonate.

All these methods have been employed by various chemists, some recommending one and some another. Knorre and Arndt,[2] in their work on the oxidation-products of hydroxylamine, use permanganate, and Lainer,[3] in his photographic work with hydroxylamine, employs the same reagent. This method was tested and found to be inaccurate. The amount

[1] Ber. d. chem. Ges., **10**, 1940.
[2] *Ibid.*, **33**, 30.
[3] Dingler: Polytech. J., **276**, 521.

of permanganate necessary for the titration was found to vary with the amount of ferric sulphate present, the length of time the solution was heated with the hydroxylamine, and the rapidity with which the permanganate was added.

Titration with free iodine in the presence of bicarbonate of sodium is used by Haga,[1] but this method has some defects. He finds that extreme dilution, or presence of carbonic acid, brings the results too high. The presence of other salts also influences the accuracy. In the present work the best results were obtained by titrating with standard iodine solution in the presence of sodium phosphate. When too great dilution is avoided and the relative proportions of the hydroxylamine and the sodium phosphate are kept fairly constant, concordant results are obtained. Wherever it was possible, however, the hydroxylamine was calculated indirectly from the nitrogen, which was determined by the Dumas method. The titration method was used to prove only that the nitrogen is not present as ammonia.

The behavior of mercury salts towards hydroxylamine was first investigated by Dresler and Stein,[2] who tried the action of hydroxylamine on mercuric oxide and obtained free mercury, and Lossen,[3] who found that mercuric chloride was rapidly reduced by the same means. There is no doubt that this is true under certain conditions, but by varying the temperature and solvent several compounds of mercury with hydroxylamine may be obtained. A salt,

$$HgSO_4.(NH_2OH)_2.H_2O,$$

prepared by the action of hydroxylamine on mercuric sulphate, corresponds closely to the salts of cobalt, manganese, and nickel prepared by Feldt[4] and Uhlenhuth.[5] The chlorides of hydroxylamine and mercury, on the other hand, seem, as a rule, more complex. Crismer[6] and other chemists have prepared chlorides of zinc, cadmium, barium, cobalt, and manganese with hydroxylamine of crystallization. These com-

[1] J. Chem. Soc. (London), **51**, 794.
[2] Ann. Chem. (Liebig), **150**, 242.
[3] *Ibid.*, Supp.-Bd., **6**, 220.
[4] Ber. d. chem. Ges., **27**, 401.
[5] Ann. Chem. (Liebig). **307**, 332.
[6] Bull. Chem. Soc., [3], **3**, 114.

pounds have the general formula $MCl_2(NH_2OH)_2$. Feldt,[1] in his effort to prepare the corresponding salt of mercury confirmed the statement of Lossen, Dressler, and others, that on account of the reducing action of hydroxylamine and the easy reduction of mercuric chloride, no stable addition-product is obtained. By modifying conditions of temperature and solvent, however, I have prepared and isolated a number of chlorides of mercury and hydroxylamine. The simplest of these, $HgCl_2(NH_2OH)_2$, corresponds in composition to the general type of the chlorides mentioned above. Further work, however, may show that it is analogous to the mercuramines. It forms a double salt with normal hydroxylamine hydrochloride, $HgCl_2.(NH_2OH)_2(NH_2OH.HCl)_2$, and also a double salt with dibasic hydroxylamine hydrochloride,

$$HgCl_2(NH_2OH)_2(NH_2OH)_2HCl.$$

Besides these, a double salt of mercuric chloride with normal hydroxylamine hydrochloride, $HgCl_2(NH_2OH)HCl$, has been obtained, as well as a stable compound which may be mercuric chloride with dibasic hydroxylamine hydrochloride, $2HgCl_2.5(NH_2OH)_2HCl$, though it is probably much more complex.

Thinking that the other halogen salts of mercury and hydroxylamine might be less complex, I attempted to prepare them, but no compound with mercury and iodine was obtained, and only one bromide,

$$HgBr_2(NH_2OH)_2(NH_2OH.HBr)_2,$$

was prepared. The hydrobromide and hydriodide of hydroxylamine have a stronger reducing action upon mercury than the corresponding chloride, and they also appear to have less tendency to form complex salts. While Lossen[2] made a number of salts of hydroxylamine, and other chemists have since added to the number, no account of the hydrobromide has been given. Piloty and Ruff[3] prepared the tribasic hydroxylamine hydriodide, and Dunstan and Golding[4] made

[1] *Loc. cit.*
[2] Ann. Chem. (Liebig), Supp.-Bd., **6**, 220.
[3] Ber. d. chem. Ges., **30**, 1656.
[4] J. Chem. Soc. (London), **69**, 839.

the dibasic hydriodide, but they were unable to obtain the normal hydriodide. I have prepared both the normal, $NH_2OH.HBr$, and the dibasic, $(NH_2OH)_2HBr$, hydroxylamine hydrobromides as well as the normal hydroxylamine hydriodide, $NH_2OH.HI$. As no double bromides or iodides of hydroxylamine with metallic salts corresponding to the general formula, $MX_2(NH_2OH)_2$, had been prepared, and since their action on mercury is too violent to separate any intermediate products of the reaction, it seemed desirable to study the action of hydroxylamine hydriodide and hydrobromide on cadmium salts, which, though similar to those of mercury, are less easily reduced. The compounds $CdBr_2(NH_2OH)_2$ and $CdI_2(NH_2OH)_2$ were readily obtained from this reaction.

Many experiments in this work required the use of pure, dry hydroxylamine. This was made from the phosphate by distillation according to the method of Uhlenhuth.[1]

EXPERIMENTAL PART.

Hydroxylamine sulphate, the starting point in the preparation of all the salts described below, is made according to the directions of Divers and Haga.[2] The following slight modifications, however, are observed in carrying out their method:

1. A constant supply of gas for sulphonating is obtained by using liquid sulphur dioxide confined in siphons.

2. If the solution into which the sulphur dioxide is being led contains 2 or less molecules of sodium carbonate to 1 molecule of sodium nitrite, the entire solution may decompose toward the end of the reaction, even though the vessel containing the solution is immersed in brine and ice. To avoid this a solution containing sodium carbonate in slight excess of the molecular proportions is employed. It was also found that, even if by mistake too little sodium carbonate has been added at the beginning, the decomposition could be arrested, if, as soon as the solution began to turn brown, sodium carbonate was added and sulphur dioxide run in until the solution became colorless. Taking these precautions the solution remains clear when it becomes acid, and may be warmed up rapidly with perfect safety.

[1] Ann. Chem. (Liebig), 311, 117.
[2] *Loc. cit.*

3. After hydrolysis of the sodium oxamidosulphonate, $NH(OH)(SO_3Na)$, and the neutralization of the resulting sulphuric acid with sodium carbonate, it was found convenient to first cool the solution to zero and separate the principal portion of the sodium sulphate by crystallization, then to evaporate the remaining solution to such a volume that 1 cc. contains 0.25 gram of hydroxylamine sulphate, finally to cool this solution to —8°, and to remove the sodium sulphate which crystallizes. By this separation of the sodium sulphate into two portions the bulk of the solution is quickly reduced, the first and largest yield of sodium sulphate crystals is easily separated from hydroxylamine, and a concentrated solution of hydroxylamine sulphate is obtained which may be cooled to —8° without freezing.

4. The final concentration of the solution containing the hydroxylamine sulphate is carried out at diminished pressure, thereby avoiding local superheating and decomposition.

Dry hydroxylamine sulphate is insoluble in absolute alcohol and almost insoluble in 95 per cent alcohol.

As in the course of this work it was necessary to know approximately the solubility of hydroxylamine sulphate in water at various temperatures, the following table, giving the amount of hydroxylamine sulphate in 1 gram water solution, was worked out; absolute accuracy was not attempted:

Temperature.	Grams of hydroxylamine sulphate.
—8°	0.307
0	0.329
10	0.366
20	0.413
30	0.441
40	0.482
50	0.522
60	0.560
90	0.685

Hydroxylamine Phosphate.—The phosphate of hydroxylamine is about one-twentieth as soluble in water at the ordinary temperature as the sulphate; hence when normal sodium phosphate is added to a concentrated solution of hydroxylamine sulphate, the phosphate separates in crystalline form,

and it can be readily purified by recrystallization. Its solubility in water is as follows, the amount of the salt in 1 gram of the water solution being given :

Temperature.	Grams of hydroxylamine phosphate.
0°	0.012
10	0.015
20	0.019
30	0.027
40	0.040
50	0.055
60	0.077
70	0.102
80	0.133
90	0.168

The difference in solubility between the phosphate and sulphate may be utilized to work up the mother-liquor and wash-waters from which the sulphate will no longer crystallize.

In the preparation of the sulphate by the Divers and Haga method, after two or three crops of crystals have been separated, there remains a viscous mother-liquor containing considerable hydroxylamine sulphate mixed with sodium sulphate, with impurities which were contained in the original crude materials, and with decomposition-products formed during the hydrolysis. From this mixture normal sodium phosphate precipitates a considerable amount of hydroxylamine phosphate.

The normal sodium phosphate for this purpose is readily prepared by adding the calculated quantity of sodium hydroxide to acid sodium phosphate. Including both the sulphate and phosphate, the yield of hydroxylamine obtained by this method is even better than that reported by Divers and Haga. Nine hundred grams of sodium nitrite gave 700 grams of sulphate and 80 grams of phosphate of hydroxylamine.

Hydroxylamine Hydrochloride, $NH_2OH.HCl$. — Eickhoff[1] states that if the calculated quantity of barium chloride be added to hydroxylamine sulphate in water solution and the barium sulphate removed by filtration, the hydroxylamine hydrochloride may be separated by concentration and crystal-

[1] J. Pharm., [5], **21**, 245-246; Abstr. in J. Chem. Soc. (London), **58**, 558 (1890).

lization. This method is difficult to carry out and the yield is poor. When either reagent is in excess double salts are formed, and if the hydroxylamine sulphate contains any impurities it is not easy to calculate the exact quantity of the chloride required for neutralization.

The following modification of the process is found to be much more satisfactory: Barium chloride is added in slight excess to a water solution of hydroxylamine sulphate, the solution filtered free from barium sulphate, and evaporated to dryness on a water-bath. The residue is placed in a Soxhlet apparatus and extracted with alcohol, the insoluble barium chloride remaining in the apparatus. The hydroxylamine hydrochloride, being only moderately soluble in alcohol, soon crystallizes in the distilling-flask, and that remaining in solution is easily obtained by evaporating the alcohol.

If chemically pure hydrochloride is desired, absolute alcohol should be used, taking precautions to exclude moisture, but for most purposes 95 per cent alcohol is satisfactory. The hydrochloride obtained in this way contains only a slight trace of barium. The phosphate being relatively insoluble in water can be easily purified by crystallization, and is also converted into the hydrochloride by the above process. This method is found convenient for reclaiming residues of hydroxylamine and reconverting them into the hydrochloride.

Hydroxylamine Hydrobromide, $NH_2OH.HBr$.—This salt is obtained as follows: Barium bromide is added to hydroxylamine sulphate in water solution, keeping the sulphate in slight excess, as barium bromide is not insoluble in alcohol. After filtering, the solution is evaporated to dryness on the water-bath, the residue dried in a vacuum desiccator over calcium chloride for forty-eight hours and extracted with absolute alcohol. On cooling the solution, large, well-formed, white, acicular crystals of hydroxylamine hydrobromide are deposited. A further yield of the salt is obtained, either by evaporating the alcoholic solution or by precipitating with ether. When the hydrobromide is precipitated from its alcoholic solution by ether, the crystals formed are shorter and the bases more prismatic than when crystallized by evapora-

tion. This salt is very soluble in water, insoluble in ether; pure and dry it is stable if kept in glass-stoppered bottles. In the presence of impurities it decomposes slowly in the light, becoming yellowish-brown in color. It is a stronger reducing agent than the corresponding hydrochloride.

I. 5 cc. solution containing 0.03135 gram substance required 6.8 cc. standard iodine solution (1 cc. iodine solution equals 0.00133 gram hydroxylamine).

II. 0.2913 gram substance gave 0.4799 gram AgBr and 0.0627 gram gave, on titration, 0.0182 gram hydroxylamine.

	Calculated for $NH_2OH.HBr$.	Found. I.	II.
Br	70.17	....	70.09
NH_2OH	29.02	28.86	28.92

Dibasic Hydroxylamine Hydrobromide, $(NH_2OH)_2HBr$.—This salt is prepared by adding free hydroxylamine to a concentrated alcoholic solution of the normal hydroxylamine hydrobromide. It separates as well-formed, white, plate-like crystals. A second crop of crystals separates upon the addition of a little ether to the filtrate. This compound is less soluble in alcohol at ordinary temperature than the normal salt. It is insoluble in ether and ligroin, very soluble in water. It acts as a strong reducing agent, and under normal conditions its properties are very similar to those of the corresponding dibasic hydrochloride. Analysis shows it to be $(NH_2OH)_2.HBr$.

0.2065 gram substance gave 0.2671 gram AgBr.

0.0513 gram required 17.3 cc. iodine solution.

	Calculated for $(NH_2OH)_2.HBr$.	Found.
Br	54.42	54.54
NH_2OH	44.89	44.87

Various proportions of free hydroxylamine were added to solutions of normal hydroxylamine hydrobromide in water and alcohol in an effort to prepare salts corresponding to the tribasic hydrochloride described by Lossen,[1] and the tribasic hydriodide prepared by Piloty and Ruff,[2] but without success.

[1] Ztschr. Chem. (N. F.), 7, 326.

[2] *Loc. cit.*

Hydroxylamine Hydriodide, $NH_2OH.HI$.—Dunstan and Golding[1] obtained the dibasic and tribasic hydroxylamine hydriodide by the action of methyl iodide on hydroxylamine dissolved in methyl alcohol. They also prepared both these salts by the direct combination of hydroxylamine and hydriodic acid, but when they attempted to prepare the normal hydriodide by mixing the calculated quantity of an alcoholic solution of hydroxylamine with aqueous hydriodic acid, the solution quickly darkened in color, and when it was evaporated either by heating it or by placing it in a desiccator over sulphuric acid, further decomposition occurred. Several other methods for preparing the hydriodide were tried by them without success.

Wolfenstein and Groll[2] have succeeded in making the normal hydriodide by treating free hydroxylamine with a water solution of hydriodic acid and evaporating the solution under diminished pressure. Their method was published after my work was done and it is, I believe, less satisfactory than mine, both as to the ease with which the operation is carried out and also in the yield obtained.

Normal hydroxylamine hydriodide is made by treating a solution of hydriodic acid in dry, low-boiling ligroin with pure hydroxylamine. Ligroin is chosen for this purpose as hydriodic acid attacks alcohol and ether. In making the hydriodic acid by the Lothar Meyer[3] method much time may be saved by keeping the flask containing the moistened iodine in ice-water while the phosphorus is being added. The addition of the phosphorus, which by the old method required a half hour or more, may in this way be accomplished in a few minutes. After the phosphorus is added the mixture is warmed to 40° or 45°, when a steady stream of gaseous hydriodic acid is evolved. This gas is thoroughly dried over calcium iodide[4] and phosphorus pentoxide, then conducted into dry ligroin at zero. On adding dry hydroxylamine to this solution, a violent reaction takes place and there is imme-

[1] *Loc. cit.*

[2] Ber. d. chem. Ges., **34**, 2417.

[3] *Ibid.*, **20**, 3381.

[4] If calcium chloride is used as a drying agent, hydrochloric acid is found in the ligroin solution.

diately formed a white, crystalline precipitate of normal hydroxylamine hydriodide.

A direct analysis of the salt was not made, but after washing it thoroughly with ligroin it was dissolved in water and the proportion of the iodine to the hydroxylamine was found to be 1 molecule of hydroxylamine to 0.996 atom of iodine, which corresponds to the formula $NH_4OH.HI$ of the normal hydriodide.

10 cc. of a solution of the substance gave 0.7516 gram AgI, and 10 cc. of the same solution required 80.2 cc. iodine solution.

At the summer temperature this salt is very unstable, decomposing slowly under dry ligroin; even when placed over calcium chloride it gives off hydriodic acid and turns brown. It takes up moisture from the air and liquefies in a short time. Its water solution almost immediately turns light yellow in color because of a slight decomposition. It dissolves somewhat in ether, but the solution soon becomes cloudy and deposits dibasic hydroxylamine hydriodide. This reaction takes place much more rapidly if the hydroxylamine hydriodide is first dissolved in alcohol and ether is then added to the solution. When treated in this way, well-formed crystals of the dihydroxylamine hydriodide separate immediately and the solution becomes light-yellow in color. When free hydroxylamine is treated with a solution of ethyl iodide made by passing dry hydriodic acid into ether, according to the method of Silva,[1] there is formed dihydrohydroxylamine hydriodide with a considerable quantity of the tribasic hydriodide.

An attempt was made to prepare the normal hydroxylamine hydriodide by treating hydroxylamine sulphate in water solution with barium iodide, following out a method analogous to that by which the hydrochloride and hydrobromide have been prepared, but without success. The color and properties of the solution indicate that the salt was formed, yet when the solution was evaporated, either on the water-bath or under diminished pressure, it became dark in color, and when it was brought finally to dryness there remained free iodine mixed with crystals of some substance that was apparently the di-

1 J., (1875), p. 250.

hydroxylamine hydriodide.[1] Not much work was done on this as the other method is much more satisfactory.

Sulphate of Mercury and Hydroxylamine, $HgSO_4(NH_2OH)_2H_2O$.—This salt is prepared by two methods:

1. To freshly precipitated mercuric oxide, washed free from alkali, hydroxylamine sulphate is added in considerable excess. When the mixture is vigorously shaken, the mercuric oxide dissolves entirely, producing a clear solution from which crystals soon separate. Care is taken to keep the solution cold and to avoid an excess of mercuric oxide.

2. To dry mercuric sulphate a 10 per cent solution of hydroxylamine sulphate in water is added and this mixture vigorously agitated, and then rapidly decanted from any undissolved mercuric sulphate. The clear liquid yields, on standing, crystals of the same salt as those made from the mercuric oxide. The crystals obtained by either of the above methods are purified by washing repeatedly with water acidified with sulphuric acid, and dried over phosphorus pentoxide.

Properties.—The salt is decomposed even in the cold by water, first turning a reddish-yellow and finally black. It may be kept in a desiccator over sulphuric acid, in the dark, for some time without undergoing any apparent change, but becomes colored upon exposure to light. When cold, it keeps under a solution containing a little free sulphuric acid or hydroxylamine sulphate, but when warmed to 55° it decomposes rapidly.

I. 0.3732 gram substance gave 0.1963 gram Hg.
0.2750 gram substance gave 0.1700 gram $BaSO_4$.
0.4387 gram substance gave 29 cc. N at 22° and 731.1 mm. (corr.)[2].

II. 0.4886 gram substance gave 0.2556 gram Hg.
0.4519 gram substance gave 0.2774 gram $BaSO_4$.

[1] The work described here was carried on during the month of July, when the temperature was between 30° and 40° and the atmosphere almost saturated with water vapor. In evaporating at diminished pressure a temperature below 30° was not obtained. The method is similar to that successfully employed by Wolfenstein and Groll.

[2] Corrected for vapor-tension over 30 per cent caustic potash.

0.3812 gram substance gave 24 cc. N at 22° and 732.2 mm. (corr.).

III. 0.4705 gram substance gave 0.2467 gram Hg.
0.1822 gram substance gave 0.1117 gram $BaSO_4$.

	Calculated for $HgSO_4(NH_3OH)_2.H_2O$.	Found. I. Made from oxide.	II.	III. Made from sulphate.
Hg	52.63	52.57	52.51	52.41
SO_4	25.26	25.48	25.29	25.28
N	7.36	7.36	7.09	....

Chlorides of Mercury and Hydroxylamine, $HgCl_2(NH_3OH)_2$. —The compound $HgCl_2(NH_3OH)_2$ is prepared by the following methods:

1. A cold alcoholic solution of hydroxylamine is added, drop by drop, to a thoroughly agitated solution of mercuric chloride in absolute alcohol, which is cooled to —10°.

2. Free hydroxylamine is added, drop by drop, to a mixture of 4 parts of mercuric chloride and 1 part hydroxylamine hydrochloride, dissolved in alcohol, which is cooled to —10°.

On allowing the solutions produced by either of the above methods to remain cold for a few minutes, white microscopic crystals of $HgCl_2(NH_3OH)_2$, mixed with mercurous chloride and double salts of $HgCl_2(NH_3OH)_2$ with hydroxylamine hydrochloride, separate. By filtering, washing, and redissolving in absolute alcohol, to which has been added a trace of hydroxylamine hydrochloride, long, white, acicular crystals of $HgCl_2(NH_3OH)_2$ are obtained. The second of the above methods gives the better results, as there is less mercurous chloride formed.

I. 0.2152 gram substance gave 0.1290 gram Hg.
0.2977 gram substance gave 0.2495 gram AgCl.
0.3453 gram substance gave 23.8 cc. N at 17° and 735.2 mm. (corr.).

II. 0.0945 gram substance gave 0.0560 gram Hg.
0.1718 gram substance gave 0.1467 gram AgCl.
0.2054 gram substance gave 15 cc. N at 18° and 740.2 mm. (corr.).

	Calculated for $HgCl_2(NH_2OH)_2$.	Found. I. Salt made by 1st method.	Found. II. Salt made by 2nd method.
Hg	59.34	59.98	59.25
Cl	21.06	20.97	21.11
N	8.39	7.97	8.21

This substance is fairly soluble in methyl or ethyl alcohol, from which solution it may be precipitated by ether. On standing in absolute alcohol there is considerable reduction even in the cold, while on warming the reduction is much more rapid. The stability of this salt is increased by the presence of a small quantity of hydroxylamine hydrochloride. Sodium hydroxide decomposes it rapidly. It is insoluble in ether, but readily soluble in a water solution of hydroxylamine hydrochloride, with which it probably forms a double salt. It is immediately decomposed by water into mercurous chloride. The crystals keep their shape, although, under a microscope, they are found to be lusterless and porous. When fresh crystals of this substance are dissolved in alcohol or a water solution of hydroxylamine hydrochloride, and ammonia is added to the solution, a white precipitate is formed which becomes black on standing a few minutes in the cold, or immediately on warming. This change of color is accompanied by an evolution of gas, and finally gray metallic mercury collects.

$HgCl_2(NH_2OH)_2(NH_2OH.HCl)_2$.—One molecule of mercuric chloride and 2 molecules of hydroxylamine hydrochloride are dissolved in absolute methyl alcohol, cooled down to —10°, and 2 molecules of free hydroxylamine are added, as in the method described in the previous experiment. A white, crystalline substance is thus obtained which in form differs from that previously described. The crystals are much more dense, and may be recrystallized from methyl alcohol without change of composition, as is shown by analysis II. below. They are soluble in ethyl and methyl alcohol, and appear to be the most stable of any of the mercury compounds here described, yet upon warming considerable decomposition takes place. They are unstable in the presence of alkalies, either in a solution of water or alcohol.

I. 0.3132 gram substance gave 0.1336 gram Hg.
0.2372 gram substance gave 0.2843 gram AgCl.
0.3410 gram substance gave 36.2 cc. N at 16° and 731.2 mm. (corr.).

II. 0.1456 gram substance gave 0.0615 gram Hg.
0.2224 gram substance gave 0.2669 gram AgCl.

	Calculated for $HgCl_2(NH_2OH)_2(NH_2OH.HCl)_2$.	Found. I. Crude.	II. Recrystallized.
Hg	42.12	42.67	42.28
Cl	29.83	29.64	29.68
N	11.77	12.16	....

$HgCl_2(NH_2OH)_2(NH_2OH)_2HCl$.—One molecule of mercuric chloride and 1 molecule of hydroxylamine hydrochloride are dissolved in methyl alcohol, cooled to —10°, and 3 molecules of free hydroxylamine contained in a concentrated solution of cold methyl or ethyl alcohol are slowly added with constant shaking. The solution remains clear for a few minutes, but when left standing for half an hour in brine and ice a considerable quantity of white crystals, which under the microscope appear uniform, separates. This salt is soluble in methyl- and ethyl alcohol. Water also dissolves it completely, but the solution becomes turbid on standing a few minutes.

I. 0.2284 gram substance gave 0.1043 gram Hg.
0.2094 gram substance gave 0.2036 gram AgCl.
0.2610 gram substance gave 29.4 cc. N at 20° and 728 mm. (corr.).

II. 0.2365 gram substance gave 0.1078 gram Hg.
0.2802 gram substance gave 0.2751 gram AgCl.
0.4692 gram substance gave 49.8 cc. N at 19° and 741 mm. (corr.).

	Calculated for $HgCl_2(NH_2OH)_2(NH_2OH)_2HCl$.	Found. I. From methyl alcohol.	II. From ethyl alcohol.
Hg	45.50	45.68	45.58
Cl	24.23	23.96	24.28
N	12.74	12.66	12.24

An attempt to recrystallize this substance from alcohol

shows that on warming there is considerable reduction into mercurous chloride, and when the solution is filtered and cooled, long, white crystals are obtained which, when analyzed, prove to be $HgCl_2(NH_2OH)_2$.

In analyzing the compound

$$HgCl_2(NH_2OH)_2(NH_2OH)_2HCl,$$

approximately one-half of the nitrogen is driven off at a low temperature, while to expel the remainder it is necessary to elevate the temperature very considerably, which indicates that the nitrogen is held bound in two different combinations which are expressed by the double-salt formula given above.

Other double salts of this nature were obtained, but when an attempt was made to purify them they decomposed completely or changed into the more stable forms before they could be separated.

Double Chloride of Mercury and Hydroxylamine, $HgCl_2(NH_2OH)HCl$. — Hydroxylamine hydrochloride increases the solubility of mercuric chloride in alcohol or water, and a double salt is prepared by mixing hydroxylamine hydrochloride and mercuric chloride in the proportion of 1 molecule of each dissolved in as small an amount of water as possible. The solution is then placed over calcium chloride. In a few days white crystals of a double salt,

$$HgCl_2.(NH_2OH)HCl,$$

separate. The salt thus obtained is filtered by suction and dried on blotting-paper. Owing to its extreme solubility in both alcohol and water, it is difficult to purify. It is less soluble in ether, but when the solution is evaporated it separates as an oil and not as crystals. A sample left exposed to the air absorbed water and liquefied in an hour.

0.4585 gram substance gave 0.2710 gram Hg.

0.3712 gram substance gave 0.4719 gram AgCl.

0.7132 gram substance gave 24.3 cc. N at 17° and 738 mm. (corr.).

	Calculated for $HgCl_2(NH_2OH)HCl$.	Found.
Hg	58.73	59.10
Cl	31.25	31.98
N	4.11	3.94

When mercuric chloride is added to hydroxylamine hydrochloride in excess of the proportion of 1 : 1, and the solution is evaporated, mercuric chloride separates from the hydroxylamine; and when in a proportion of less than 1 : 1, hydroxylamine hydrochloride separates free from mercury. If other salts are formed they dissociate upon concentration and cannot be obtained in this way. Hydroxylamine hydrochloride is almost insoluble in absolute ether. An attempt was made to prepare double salts by using ether as a solvent for mercuric chloride and adding powdered hydroxylamine hydrochloride to the solution in various proportions, but without success, for when 2.2 grams of hydroxylamine hydrochloride are added to 4.4 grams of mercuric chloride dissolved in 300 cc. of absolute ether, only 0.32 gram of hydroxylamine hydrochloride is dissolved after shaking the mixture for three days. When a small quantity of alcohol is present the solubility of the hydroxylamine hydrochloride is greatly increased, and when ligroin is added a voluminous white precipitate is produced. Analysis shows this to be a mixture which proved so unstable that no definite pure salt could be obtained.

$2HgCl_2.5(NH_3OH)_2HCl$.—This appears to be the most easily prepared of any of the mercury and hydroxylamine compounds here described. Apparently, whenever mercuric chloride is present in solution with excess of hydroxylamine hydrochloride and free hydroxylamine, this salt is formed. The compound, besides occurring as a by-product in several other experiments, is prepared in the following ways:

1. There is added to freshly prepared mercuric oxide, suspended in ethyl alcohol, a solution of hydroxylamine hydrochloride in ethyl alcohol. Both liquids are cooled down to —10° in brine and ice, mixed while cold, shaken thoroughly, and decanted from the undissolved mercuric oxide. The clear solution, on standing a few minutes, deposits flat, hexagonal crystals which must be immediately separated from the solution containing undissolved mercuric oxide. If they are left in contact with the oxide, reduction begins at once and spreads rapidly through all the crystals, leaving, finally, metallic mercury. By keeping the temperature below zero

this decomposition is retarded, but not wholly prevented. The crystals thus obtained are further purified by recrystallization from absolute alcohol (see Analysis I.).

2. A solution of hydroxylamine hydrochloride in methyl alcohol is added to mercuric oxide suspended in methyl alcohol. Crystals separate, similar in appearance to those separating from ethyl alcohol. The salt is more soluble in methyl alcohol than in ethyl alcohol, and decomposes more easily in the presence of the former. For the composition of these crystals see analysis II.

3. Two parts of free hydroxylamine are added to a mixture, in alcohol, of 1 part of mercuric chloride with 6 of hydroxylamine hydrochloride; by keeping all the solutions below zero, crystals similar to those previously described separate. They are purified by recrystallization. It will be seen that this method is similar to that used by Hofmann[1] for preparing his mercuramines (analysis III.).

4. The alcoholic filtrate from which the first crop of crystals separates contains in solution a considerable quantity of the same salt which may be precipitated by adding ether. The crystals thus formed are similar to those previously obtained (analysis IV.).

5. This same salt of mercury is obtained by adding a solution of hydroxylamine hydrochloride in water to mercuric oxide; but on account of the solubility of the salt, as well as its instability in water, this method is less satisfactory than those previously described.

I. 0.4425 gram substance gave 0.1680 gram Hg.
0.4752 gram substance gave 0.5860 gram AgCl.
0.4860 gram substance gave 55 cc. N at 20° and 737 mm. (corr.).

II. 0.5078 gram substance gave 0.1931 gram Hg.
0.3883 gram substance gave 0.4771 gram AgCl.
0.3246 gram substance gave 38 cc. N at 19° and 740.1 mm. (corr.).

III. 0.2488 gram substance gave 0.0938 gram Hg.
0.2085 gram substance gave 0.2587 gram AgCl.

[1] *Loc. cit.*

0.2385 gram substance gave 28.1 cc. N at 21°.5 and 733 mm. (corr.).

IV. 0.1718 gram substance gave 0.0651 gram Hg.
0.2129 gram AgCl.

	Calculated for $2HgCl_2.5(NH_3OH)_2HCl$.	Found. I.	II.	III.	IV.
Hg	37.95	37.96	38.02	37.72	37.88
Cl	30.26	30.28	30.38	30.48	30.29
N	13.28	12.48	13.17	13.28	....

The salt is soluble in water at the ordinary temperature with gradual reduction to mercurous chloride. When ammonium hydroxide is added to a water solution, a white precipitate is formed which turns black gradually in the cold, and rapidly when heated. It is soluble in alcohol and ether; in the presence of mercuric oxide it decomposes slowly at —10°, and rapidly at higher temperatures. It is soluble in hydrochloric acid. The slightest trace of alkali causes decomposition.

Some experiments were carried out with mercurous chloride and hydroxylamine to determine whether a reaction takes place between them, but owing to the insolubility of the mercurous chloride no definite results were obtained. Freshly precipitated mercurous chloride, when treated with a solution of hydroxylamine hydrochloride, was found to be slightly soluble in it, but no combination of the two was observed. Mercurous chloride, when boiled with free hydroxylamine in methyl alcohol in a flask fitted with a return condenser, was reduced gradually to metallic mercury. In the cold the reduction takes place very slowly.

Mercuric Bromide and Hydroxylamine.—When mercuric oxide is treated with a solution of normal hydroxylamine hydrobromide in an alcoholic solution cooled below zero, it dissolves, and if the solution is kept cool there separate white, well-formed crystals of dihydroxylamine hydrobromide. The solution contains mercuric bromide, which can be separated. The reaction is probably represented by the following equation:

$$HgO + 4NH_2OH.HBr = HgBr_2 + 2(NH_2OH)_2HBr + H_2O.$$

This is in marked contrast with the action of hydroxylamine hydrochloride on mercuric oxide.

$HgBr_2(NH_2OH)_2.(NH_2OH.HBr)_2$.—This compound is made by mixing mercuric bromide and normal hydroxylamine hydrobromide in the proper molecular proportions in methyl alcohol, cooling the mixture below zero, and adding to it, drop by drop, a solution of free hydroxylamine in methyl alcohol. On the addition of ether a white precipitate is formed, which is filtered and washed thoroughly with ether, care being taken to keep the salt cold. Analysis shows it to be $HgBr_2(NH_2OH)_2.(NH_2OH.HBr)_2$. It crystallizes in microscopic, quadratic plates. It is soluble in methyl alcohol with slow decomposition. The water solution becomes cloudy on standing a few minutes, indicating a reduction to mercurous bromide. It is readily decomposed by alkalies and is less stable than the corresponding chloride.

0.3911 gram substance gave 0.1189 gram Hg.

0.2879 gram substance gave 0.3326 gram AgBr.

0.1838 gram substance gave 14.4 cc. at 28° and 726.2 mm. (corr.).

	Calculated for $HgBr_2(NH_2OH)_2.(NH_2OH.HBr)_2$.	Found.
Hg	30.58	30.42
Br	48.93	49.16
N	8.56	8.84

Methods similar to those by which $HgCl_2(NH_2OH)_2$ was obtained were tried to prepare the corresponding bromide, but without success.

Mercuric Iodide and Hydroxylamine.—When mercuric oxide was treated with hydroxylamine hydriodide the reduction to metallic mercury was so rapid, even in the cold, that no intermediate products could be separated.

Mercuric iodide was dissolved in alcohol and cooled below zero; to this solution hydroxylamine hydriodide was added. Yellow crystals of pure mercurous iodide soon separated. Attempts were made to precipitate some salt from the solution with ether and ligroin before the mercurous iodide separated, but without success. When these results are compared with

those obtained with the hydroxylamine hydrochloride and hydrobromide, an increase in reducing power from the hydrochloride to the hydriodide is noted.

Cadmium Bromide and Hydroxylamine.—Hydroxylamine combines with neither mercuric iodide nor bromide to form stable salts of the general formula $MX_2(NH_2OH)_2$. Attention was turned, therefore, toward cadmium, since its salts are in some respects similar to mercury, yet less easily reducible. Cadmium bromide was dissolved in alcohol, and to the solution free hydroxylamine was added. There was immediately formed a fine, white, crystalline precipitate of $CdBr_2(NH_2OH)_2$. This salt dissolves in hot water, forming in a few minutes a white, basic salt. It is readily soluble in dilute acids, insoluble in alcohol and ether.

0.2316 gram substance gave 0.1418 gram $CdSO_4$.

0.3965 gram substance gave 0.4404 gram AgBr.

0.0546 gram substance gave, on titration, 0.0105 gram NH_2OH.

0.3252 gram substance gave 24.6 cc. N at 27° and 721 mm. (corr.).

	Calculated for $CdBr_2(NH_2OH)_2$.	Found.
Cd	33.13	32.94
Br	47.33	47.26
NH_2OH	19.52	19.22
N	8.28	8.13

Cadmium Iodide and Hydroxylamine, $CdI_2(NH_2OH)_2$.—Pure hydroxylamine is added to a strong solution of cadmium iodide in alcohol. A precipitate, which dissolves readily, is formed when the addition is first made; but on allowing the solution to stand there separate large, colorless, acicular crystals of $CdI_2(NH_2OH)_2$.

0.2886 gram substance gave 0.1284 gram $CdSO_4$.

0.4155 gram substance gave 0.4185 gram AgI.

0.0916 gram substance gave, on titration, 0.0197 gram NH_2OH.

0.2456 gram substance gave 20.4 cc. N at 26° and 722 mm. (corr.).

	Calculated for $CdI_2(NH_2OH)_3$.	Found.
Cd	24.08	23.96
I	54.57	54.44
NH_2OH	21.29	21.52
N	9.03	9.08

This compound is stable, soluble in both alcohol and water, and insoluble in ether. Its formula emphasizes the tendency of iodine, already noted by Dunstan and Golding,[1] to combine with 3 molecules of hydroxylamine.

Analytical Methods.

The mercury in the preceding experiments was determined by dissolving the compounds in potassium cyanide, passing an electric current of 0.1 ampère and 2.5 volts for fourteen hours through the solution and weighing the metallic mercury.

For estimating the chlorine in those salts which are soluble without decomposition in water, the solution was slightly acidified with nitric acid and the mercury removed by means of hydrogen sulphide. By keeping it in a warm place for a few hours most of the hydrogen sulphide is driven off; silver nitrate added to the solution made alkaline with ammonia removes the remainder; then, on making the solution acid, the silver chloride is precipitated and determined in the usual manner. Though this method might have given good results with those chlorides which are insoluble or give precipitates in water, it was considered safer to heat them in a tube with calcium oxide, drive off the mercury, and determine the chlorine in the residue.

In the analysis of those salts containing sulphuric acid, a weighed quantity of the substance was fused with sodium carbonate and potassium nitrate to remove the mercury, and the residue treated with water and barium chloride in the usual manner.

I wish here to express my thanks to Dr. Felix Lengfeld, at whose suggestion and under whose careful help and guidance this work was carried out.

KENT CHEMICAL LABORATORY,
UNIVERSITY OF CHICAGO,
August 24, 1901.

[1] *Loc. cit.*

ELECTRO-AFFINITY AS A BASIS FOR THE SYSTEMATIZATION OF INORGANIC COMPOUNDS.

By R. Abegg and G. Bodländer.

In connection with the attack upon our theory which Locke[1] has recently published, we might perhaps content ourselves with the general reflection that in the domain of chemistry hardly any valuable theory exists which does not have its weak points, and yet such theories are not on this account rejected and characterized as false, or, what is much more important, as useless. The periodic classification of the elements offers, perhaps, the best illustration. No one doubts its significance, in spite of the fact that several elements either do not show at all the analogies which the system requires or show them only to a very limited extent. We will, however, take up somewhat more in detail the various objections raised in the article referred to, as it is a matter of consequence to us that our ideas be not in an unjust way misunderstood in America, where research in inorganic chemistry, from the physico-chemical point of view, is making such gratifying progress.

The facts from which we started and to which we referred at the beginning of our article were as follows: The compounds whose constituents are easily separated by electrolysis from their solutions, that is, by the application of a small potential-difference, give solutions which contain comparatively small amounts of these constituents in the form of ions. The small ionic concentration, even of saturated solutions of these compounds, may be shown either in a slight solubility, or, when the solubility is large, in a slight dissociation, or in the transformation into a complex compound. Thus, the degree of solubility and the tendency to form undissociated or complex compounds depend, to a certain extent, upon the sum of the decomposition-potentials of the constituents. The greater this is, the greater is the solubility of the salt and the smaller its tendency to enter into complex compounds.

[1] This Journal, 27, 105 (1902).

Nernst[1] has already pointed out that a limit for the solubility of a compound is set by the decomposition-potentials of its constituents. He shows that silver iodide could not form concentrated solutions since, on account of the small decomposition-potential of the iodine and the negative decomposition-potential of the silver, such solutions of it would of themselves decompose into silver and iodine. In fact, a calculation of the maximum solubilities which the three silver halides could have without being unstable, gives the following values expressed in mols per liter :

AgI.	AgBr.	AgCl.
0.007	82	37000

The actual solubilities are much smaller. However the order of the actual solubilities is the same as that of the limiting values; and the distance from these limiting values affords a measure of the stability of the three compounds. The same fact is observed when one compares the order of the actual solubilities of the iodides of the nobler metals with the order of the calculated limiting values. In general, the ionic concentrations which are actually reached show the same sequence as the limiting values. The greater, however, the difference between the two values becomes, the greater becomes the field for the influence of other causes ; and the higher the solution-tension of the ions, the more do the limiting solubilities exceed their actual solubilities. Hence, from other causes, the solubilities may increase continually without materially diminishing the stability of the compound.

If the solubilities should continue to increase with the increase of the decomposition-potential of the constituents in the same ratio as in passing from silver chloride to thallium chloride, then the halides of the alkali metals would be salts of extreme solubility ; thus, the solubility of potassium chloride would be something like 10^{60} mols per liter. Such salts would, in dissolving, set free large amounts of energy, and therefore, in the solid form, would possess a large content of free energy. In consequence of this, such salts in the solid state would form modifications which are no longer directly comparable with those of the less soluble salts.

[1] Ber. d. chem. Ges., 30, 1547 (1897).

Hence the solubility of a salt is by no means dependent solely upon the solvent and the chemical character of the salt in the dissolved state, but it depends also upon the solid modification with which the solution is in equilibrium. And one may assume that the same self-preserving law which hinders a great solubility of silver iodide, also operates to give solid potassium chloride a form less soluble than that which would be directly comparable with thallium chloride or silver chloride. In our paper we cited illustrations and called explicit attention to inversions in the order of solubilities which are ascribable to this cause. We may designate, in such cases, the solubility diminishing with increasing decomposition-potential as "inverse solubility."

The views put forward by Richards[1] give excellent evidence in favor of our suggestions concerning inverse solubilities. He states, namely, that the volumes of the chlorides of the heavy metals from zinc to silver exceed those of the corresponding metals by about 17 units, while the excess in volume in the case of magnesium is 15, of sodium only 4.2, and in the cases of potassium and rubidium it is even negative. This proves that in the latter cases there is an abnormally great contraction or association of the salt molecules corresponding to an increased energy of formation E_z in the solubility-formula of Bodländer,[2]

$$0.116 \log p = E_a + E_k - E_z,$$

where an increase of E_z obviously lowers the solubility p.

In the same sense, we find the order of the differences (Δ) between the equivalent volumes of the chlorides of the following metals and between those of the potassium salts of the halogens (see Richards' tables: *loc. cit.*, pp. 599, 602, 609) to be apparently in complete agreement with the inverse solubilities as found in these series. The values of Δ are, namely, as follows:

Chlorides:	Mg	Ca	Sr	Ba	Li	Na	K
	15.3	12.3	8.7	8.4	9.0	3.5	—7.7
		J	Br	Cl			
Potassium salts:		28.1	18.7	12.5			

[1] Ztschr. phys. Chem., **40**, 183, 597.

[2] *Ibid.*, **27**, 55; Ztschr. anorg. Chem., **20**, 460.

Besides this, the other influences which may affect the solubility of compounds of strong ions, such as the formation of hydrates and of inner complexes, are various and may operate partially in opposition to each other, so that a simple general law in the case of easily soluble compounds is not to be expected, nor did we make the assumption that such existed. We pointed out only certain regularities.

Although weak ions cannot form easily soluble salts, it is not impossible for salts formed from strong ions to be difficultly soluble. The law of self-preservation prevents the former case, but the latter fact is not inconsistent with the validity of the law. Thus, it is so self-evident that the small solubility of calcium fluoride or barium sulphate cannot be attributed to the small discharging potential of its ions that it was scarcely necessary to emphasize,—what, however, we did not neglect to call attention to,—that here influences other than the electro-affinity must come into play. When the small electro-affinity of the constituents of a salt give it a low solubility, then this small electro-affinity also causes the same substances to easily become constituents of complex salts. Thus, Locke has completely misunderstood us when he assumes that, according to our views, all substances which form insoluble compounds must also form complex compounds. This is really the case only when small electro-affinity is responsible for the insolubility of the compound. A tendency of an ion to form both slightly soluble salts and complex compounds is a proof of small electro-affinity; but, as might be expected, the electro-affinity is large where the former tendency, but not the latter one, is very marked, as in the case of the alkaline-earth metals. When the difficultly soluble substance becomes easily a constituent of a complex ion, we may perhaps consider it a direct evidence that the low solubility of the compound is due to small electro-affinity, although experimental data are here lacking.

Of course, the objection may now be raised, that one may interpret each individual case with the aid of such additional hypotheses, and we by no means hesitate to say that it is a matter of personal preference whether such additional as-

sumptions be accepted, and that the satisfactory application of them to individual cases belongs essentially to the future.

In our opinion, there is at present no single case irreconcilable with our theory, since the possible explanations for the apparent exceptions have not yet been investigated. We therefore consider our conception solely as a basis of investigation, and have published it since the application to single cases is far beyond the working ability of two men, and a general participation in the solution of inorganic problems appeared to us desirable.

We must further state in reference to the solubilities quoted by Locke that the table on page 111 contains in many places striking errors unfavorable to us. For example, zinc chromate is known only as a component of an isomorphous mixture, so that its own solubility is unknown. Barium hypophosphite, according to Wurtz,[1] is soluble in 3.5 parts of water, hence, not insoluble. Barium iodate is soluble in 3018 parts of water, zinc iodate in 114 parts,— a difference which does not justify the assertion that the former is insoluble and the latter soluble.

According to Rose,[2] zinc phosphite is more difficultly soluble than magnesium phosphite. The latter is given as difficultly soluble; nevertheless zinc sulphate causes a precipitate in its solution, so that zinc phosphite must be still less soluble. Zinc sulphite is slightly soluble, probably less so than barium sulphite. Zinc oxalate is at least as insoluble as barium oxalate, but it is of importance to note that it easily forms complex salts, which one of us is at present engaged in investigating. Barium cyanide, if free from water, dissolves, according to Joannis,[3] in 1.25 parts of water, and is extremely hygroscopic. The hydrate, with 2 molecules of water, is deliquescent.

In respect to the alums and the double salts of the type of $K_2Mg(SO_4)_2.6H_2O$, the same statements apply as in the case of the simple soluble salts. We must further take into account the fact that the solubility of such double salts, owing to

[1] Ann. chim. phys., [3], **7**, 35.
[2] Pogg. Ann., **9**, 29.
[3] Ann. chim. phys., [5], **26**, 493.

complex dissociation, the Nernst-effect (decrease of solubility by salts having a common ion), and hydrate formation in the solution, is quite a complicated phenomenon, to which it is scarcely to be expected that simple laws will apply, especially when one does not know the single factors.

In reference to the ammonia complexes of magnesium (p. 113) we may refer Locke to the work of Gaus,[1] by which their existence is proved and discussed in accordance with our theory.

The presence in a solution of salts having a common ion is the reason why thallium chloride is less soluble in chloride solutions than in water, as was long ago explained by the Nernst theory and experimentally investigated by A. A. Noyes.[2] The increase of solubility due to the formation of complexes can be expected only in the case of very great concentration of the chlorine ions; in the case of silver, a nobler metal, and hence more inclined to form complexes, this increase is only noticeable with large concentrations of the chlorine ions. This is an exact confirmation of the rule, and not a departure from it.

In regard to the complex ammonia compounds, the formulas and degrees of stability of the dissolved ions, which alone are to be considered, are still too little known. The method of Dawson and McCrae does not suffice to give information about the stability of the complexes. Besides, we must also consider that here, as in other cases, in addition to the predominating influence of electro-affinity, the individual atomic affinities come into play, in this case between the metal and ammonia.

The formation of a complex ammonia compound is only possible in the presence of an excess of free ammonia. But this gives hydroxyl ions, and whether this ammonia complex is capable of existing in detectable amounts depends not only upon its greater or less stability, but also upon the greater or less stability of the hydroxide. The stable solid compounds of ferric chloride and aluminium chloride[3] with ammonia de-

[1] Ztschr. anorg. Chem., **25**, 157 (1900).
[2] Ztschr. phys. Chem., **6**, 249 (1890).
[3] Dammer: Handbuch., III., 94. 311.

compose largely in water, while the cobalt-ammonia compound remains intact. This need not be attributed to the fact that fewer free cobalt ions and ammonia molecules exist in the presence of the cobalt-ammonia ion than with the iron-ammonia ion, but may be explained by saying that fewer ferric ions than cobaltic ions can exist in the presence of the hydroxyl ions which are formed by the ammonia. This illustrates the fact that electro-affinity which influences the solubility of the hydroxide, as well as the stability of the ammonia complex, may cause two opposite effects whose resultant cannot be foretold without further investigation. The small solubility of the basic salts in comparison with the neutral salts may be due to the fact that these dissociate according to the general formula $(M^{II}Cl)\cdot(OH)$. Here the electro-affinity leads us to expect that the basic salt be more easily soluble than the hydroxide, which agrees with the facts. The inverse solubility of the alkali salts (115) is, in our opinion, in harmony with the views given above.

In general, it appears as if it were on account of hydration that the very soluble salts deviate most from the fundamental solubility principle of our theory, and it is true that, according to the law of mass-action, the higher the concentration of the constituents which can be hydrated the greater the hydration will be.

On the other hand, the research on solubilities of difficultly soluble substances carried out by Cl. Immerwahr[1] shows a good agreement with our theory. Locke emphasizes especially, and in great detail, that the solubilities of the double salts of the type $K_2Mg(SO_4)_2.6H_2O$, of the alums, and of the double halides of caesium do not correspond with the demands of our ideas. These salts are present in solution only partially as complexes[2] and partially in the form of the single salts, and we have scarcely any information concerning their quantitative relations. Both components influence mutually the dissociation, and thus, to a great extent, the solubility, so that the total solubility of such a double salt affords no information concerning the concentration and stability of the complex ion.

[1] Ztschr. f. Elektrochemie, 7, 477.

[2] See Rieger: *Ibid.*, 7, 863, 871 (1901).

The homologous series of the alkali-chromium alums affords an evident numerical series of the solubility, but this is hardly to be considered as an objection against the presence of secondary solubility influences, for in homologous series regular gradations which underlie these secondary influences might lead to such results.

The series of objections with which Locke closes his paper seem expressly calculated to reproach us with being obscure. He avoids, however, a concrete discussion, which might be more in our favor. Thus, as a matter of fact, the iodates and periodates of metals, whose iodides are typically difficultly soluble, are more soluble than the iodides. Locke evidently expects that every reader will recall the much better known alkali compounds where the inverse solubility conditions occur, which were discussed above and in our previous article.

The greater solubility of the mercuric salts, as compared with mercurous salts, was also considered in our original paper (pp. 466–467).

The behavior of these salts completely agrees with our views, considering only their ionic concentrations, to which the theory solely applies, but by no means to the total solubility, for it is not at all improbable that the concentration of mercurous ions in a saturated solution of calomel is greater than the concentration of the mercuric ions in a saturated solution of the sublimate. The mercuric salts form complex salts easily, mercurous salts almost not at all. This agrees perfectly with the position of the metals in the order of their electrolytical potentials, since it has been shown by Ogg[1] and Abel[2] that mercuric mercury is actually more noble than mercurous mercury.

However, we do not wish to put forward our ideas as a dogma, nor to urge prematurely on the chemical world their general acceptance, but we present them as a working hypothesis, the value of which is to be measured by its fruits. We may further justify the presentation of our theory by

[1] Ogg: Ztschr. phys. Chem., **27**, 285 (1898).
[2] Abel: Ztschr. anorg. Chem., **26**, 361 (1901).

quoting from a recent paper by Richards,[1] who says: "No hypothesis has as yet been proposed which has been found completely satisfactory; our knowledge is incommensurable for all existing possibilities. However, when one finds that a certain theory explains some relations better than other hypotheses, it may serve to suggest new experimental investigations. Such a service is of course the best that an hypothesis is able to accomplish."

Inorganic chemistry requires especially for its development along physico-chemical lines broad generalizations, and we have introduced the idea of electro-affinity in the hope that it may prove to be of this character. By reason of the lack of a comprehensive theory the large domain of complex compounds is less inviting than it should be.

If, by our views, any new investigators are led to this field, which actually has been the case to some extent already, we shall consider that alone as a successful outcome, even if, in contrast to the results thus far obtained, further investigations should show that the directing effect of electro-affinity is made unrecognizable by the secondary influences present.

What Locke published against our theory, so far as it is not directly wrong, has to do with influences, which, like the partial splitting of double salts, had been known for some time, and had already been taken into consideration by ourselves. It does not, by any means, decide the question of the usefulness of our theory.

BRESLAU AND BRAUNSCHWEIG, May, 1902.

Contributions from the Chemical Laboratory of the Rose Polytechnic Institute.

XXI.—CAMPHORIC ACID.

[TWELFTH PAPER.]

SYNTHESIS OF TRIMETHYLPARACONIC ACID.

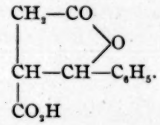
BY WILLIAM A. NOYES AND AUSTIN M. PATTERSON.

The experiments here described were undertaken for the purpose of effecting a synthesis of the camphoric acid corre-

[1] Ztschr. phys. Chem., 40, 183, 184 (1902). The conclusions which Richards draws from the consideration of the atomic volume, about the affinity between like atoms of an element offer, perhaps, a way to get from the experimentally determined electrolytical potential to what is more important for our theory, the real electro-affinity.

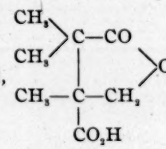
sponding to Bredt's formula for camphor. The synthesis is not completed, but enough progress has been made to make it seem desirable to publish our results.

Some years ago, Fittig and Jayne[1] showed that benzoic aldehyde and sodium succinate condense, when heated with acetic anhydride, giving phenylparaconic acid,



Later, Fittig and his students applied the reaction to include several other aldehydes, and also to include methylsuccinic acid.

So far as we are aware, no attempt has ever been made to use formic aldehyde for this reaction. We have succeeded in doing this and have effected a remarkably clean synthesis of trimethylparaconic acid,



as follows:

Trioxymethylene was prepared by evaporating a 40 per cent solution of formic aldehyde to about one-half its volume on the water-bath and drying the residue in a vacuum desiccator. About 12 grams of the dry trioxymethylene were obtained from 50 cc. of the solution. This still retains 7 to 9 per cent of water.[2] Thirteen and two-tenths grams of the sodium salt of trimethylsuccinic acid, 3.5 grams of trioxymethylene, and 9.9 grams of acetic anhydride were heated in a sealed tube at 120° to 140° for two days. The duration of the heating was probably excessive, but no experiments have been made to determine the minimum time which is allowable for the reaction. There was a slight pressure in the tube when opened. The contents dissolved easily in hot water.

[1] Ann. Chem. (Liebig), **216**, 97.
[2] Ann. chim. phys., [7], **15**, 551.

The solution was distilled with steam to remove formic aldehyde, then concentrated, acidified with hydrochloric acid, and extracted three times with ether. The residue left on distilling the ether was heated on the water-bath for some time under diminished pressure to remove acetic acid and acetic anhydride. A titration of a portion of this residue indicated that the conversion to trimethylparaconic acid was practically complete. 0.1562 gram required for neutralization 8.9 cc. of N/10 potassium hydroxide. Theory requires 9.1 cc., while the theory for trimethylsuccinic acid is 19.5 cc.

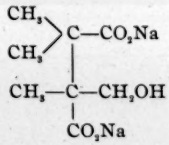
The *trimethylparaconic acid* was purified by crystallization from hot benzene, in which it is difficultly soluble. It may also be crystallized from dilute alcohol, which is a more suitable solvent for use with larger amounts. The pure acid melts with decomposition at 256° to 257°.

0.1965 gram substance gave 0.4015 gram CO_2 and 0.1209 gram H_2O.

	Calculated for $C_8H_{12}O_4$.	Found.
C	55.77	55.72
H	7.04	6.84

0.1609 gram required 9.26 cc. N/10 potassium hydroxide. Theory requires 9.35 cc.

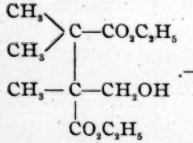
When the acid is warmed with an excess of sodium hydroxide it is converted into the sodium salt of trimethylitamalic acid,



By heating in this manner on the water-bath for twenty hours, neutralizing the solution with nitric acid, and precipitating with a slight excess of a concentrated solution of silver nitrate, a nearly quantitative conversion to the silver salt can be effected. The salt is semi-crystalline in character and difficultly soluble. The salt was dried in a vacuum desicca-

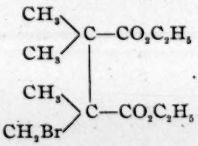
tor which was heated to 45° to 50° to hasten the process. This salt gave 53.41 per cent of silver. Theory requires 53.46 per cent.

Diethyl Ester of Trimethylitamalic Acid,

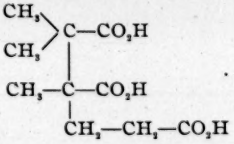


.—Twenty-three grams of the dry silver salt, 25 grams of dry ether, and 25 grams of ethyl iodide were brought together in a flask connected with an upright condenser. The reaction began spontaneously after five to ten minutes, and was continued by warming gently on the water-bath for an hour and a half. The product was filtered and the residue extracted with ether several times. Ten and seven-tenths grams of the ester were obtained, while the calculated amount is 14 grams. The ester is a viscous oil which did not solidify. An analysis of the ester from a second preparation in which less pure materials were used, was not satisfactory. We have not been able to repeat the preparation but the method used leaves little doubt of the composition of the product.

It was next desired to obtain the ethyl ester of bromtetra-



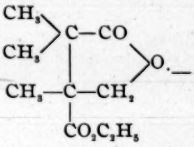
methylsuccinic acid, . By condensing this with malonic ester, saponifying the product, and splitting off carbon dioxide, it would seem possible to obtain homocam-



phoronic acid, . To obtain the brom-

ester, 10.7 grams of the diethyl ester described above were dropped into 8 grams of phosphorus tribromide carefully cooled with a freezing-mixture. The mixture was allowed to stand for two or three hours and was poured on crushed ice. The ester was separated with ether and dried *in vacuo*. In spite of the precautions taken, ethyl bromide had been split off, the resultant ester contained only a trace of bromine, and on analysis it was found to be the

Ethyl Ester of Trimethylparaconic Acid.



Analysis :

	Calculated for $C_{10}H_{16}O_4$.	Found.
C	60.00	59.23
H	8.00	8.24

The same ester was obtained by heating trimethylparaconic acid with alcohol and hydrochloric acid in a sealed tube, in the water-bath, for some hours. When prepared in this manner, it solidified on standing and then melted at 34°.5. The analysis gave : carbon, 59.81 ; hydrogen, 8.03. See above.

Whether it will be possible to overcome the difficulty encountered and obtain the ethyl ester of the bromtetramethylsuccinic acid in some other manner, it is impossible now to foresee. In any case, the work with the trimethylparaconic acid will be continued, and it is hoped that by means of it a synthesis of Bredt's camphoric acid can be effected.

TERRE HAUTE, IND.,
June 23, 1902.

THE ACTION OF LIGHT ON CINNAMYLIDENE-MALONIC ACID.

By Elmer P. Kohler.

While working with some yellow, unsaturated ketones prepared from cinnamic aldehyde I observed that they turned white when exposed to direct sunlight. The change is evidently of the same character as that observed by Liebermann[1] in the case of cinnamylidenemalonic acid, and as it seemed easier to follow such a change with an unsaturated acid than with an unsaturated ketone, I undertook a study of the acid obtained by Liebermann. The last number of the *Berichte*[2] contains an article by Riiber on the synthesis of α-truxillic acid, which, to some extent, deals with the same subject. I therefore publish the results obtained with cinnamylidenemalonic acid, reserving the work on cinnamylidene ketones for a later paper.

1. Method of Exposure.

Liebermann exposed the solid acid under a bell-jar to the direct rays of the sun and obtained almost complete transformation after two to three weeks. This method is too tedious for the preparation of larger quantities of material. The change is never complete and the product is hard to purify, as can be seen from the uncertain melting-points obtained by Liebermann. After trying a number of different conditions, I adopted the following method of procedure, which gives results that are quite satisfactory.

A solution of 20 grams of the acid, in the required amount of dilute sodium carbonate solution, is poured into an excess of dilute hydrochloric acid contained in a 3-liter balloon-flask and the liquid diluted to 2 liters. The acid is thus obtained as an impalpable yellow powder which remains suspended in the liquid for a long time. The powder changes rapidly when the flask is exposed to the direct rays of the sun, and if the flask is shaken about once an hour the change is complete

[1] Ber. d. chem. Ges., 38, 1440.
[2] *Ibid.*, 38, 2411.

after exposure of twenty to thirty hours to bright summer sunlight.

The product is separated by filtration, washed with boiling water, and dissolved, while still moist, in the minimum quantity of glacial acetic acid. On cooling this solution the substance separates in small, lustrous prisms. These are washed with acetic acid and ether and dried on the water-bath. Prepared in this way, the substance is pure white in color and melts sharply at 195°. It decomposes immediately after melting. It is readily soluble in alcohol and acetone, moderately soluble in glacial acetic acid, almost insoluble in ether, chloroform and ligroin. It crystallizes well only from glacial acetic acid.

The molecular weight, determined in acetone, showed that the substance is formed by the condensation of 2 molecules of cinnamylidenemalonic acid :

$$K = 1725.$$

Acetone. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
81.2690	1.2110	0.060	428
"	2.4320	0.128	403
"	3.3280	0.180	395
	Calculated for $(C_{12}H_{10}O_4)_2$,		436

The oxidation of the substance with potassium permanganate in alkaline solution gave essentially the same products as those obtained by Riiber. Twenty grams of the substance were dissolved in sodium carbonate solution. The resulting liquid was cooled with crushed ice and treated with 25 grams of potassium permanganate dissolved in ice-water. After standing over night in the ice-chest the oxides of manganese were removed by filtration and the filtrate acidified. The colorless acid which separated (4.9 grams) was recrystallized from methyl alcohol, from which it separated in large, colorless plates containing methyl alcohol of crystallization which was given off as soon as the crystals were removed from the mother-liquor. The substance melted at 274° and gave the following results on analysis :

I. 0.2206 gram substance gave 0.5904 gram CO_2 and 0.1080 gram H_2O.

II. 0.2004 gram substance gave 0.5353 gram CO_2 and 0.1010 gram H_2O.

	Calculated for $C_{18}H_{16}O_4$.	Found. I.	Found. II.
C	72.97	72.98	72.88
H	5.40	5.60	5.44

The substance was identified as α-truxillic acid by its melting-point and the melting-points of the methyl and ethyl esters obtained by saturating its solution in the corresponding alcohols with hydrochloric acid. It crystallizes from cold methyl alcohol with 2 molecules of methyl alcohol of crystallization.

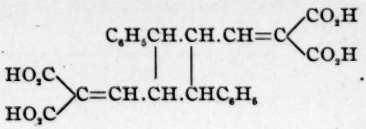
0.1220 gram substance lost 0.0198 gram at 100°.

	Calculated for $C_{18}H_{16}O_4.2CH_3OH$.	Found.
CH_3OH	16.00	16.20

The filtrate from the α-truxillic acid was extracted with ether which took up two substances: benzoic acid, identified as ethyl benzoate, and an oily acid that has not yet been obtained in pure condition.

The extracted liquid was neutralized with ammonia and treated with a solution of calcium chloride. The fine white precipitate which formed was found to be calcium oxalate.

The products of oxidation are, therefore, α-truxillic acid, benzoic acid, an oil of unknown structure, and oxalic acid. The formation of α-truxillic acid indicates that the substance contains a tetramethylene ring and leads to the formula of a diphenyltetramethylenebismethylenemalonic acid:



This formula agrees perfectly with the addition-reactions described below.

Since the change from cinnamylidenemalonic acid to a sub-

stance with this formula involves only the first set of double linkages, it seemed possible to transform some of the derivatives of the acid in the same way; but this is not the case. The sodium salt, the acid potassium salt, the methyl and ethyl esters, and the amide were exposed to the light under a variety of conditions, but no change could be detected in any of them. All of these substances are colorless while the acid is yellow, and judging by the results obtained with cinnamenyl ketones only the colored compounds are affected by sunlight. The yellow cinnamenylacetone, for example, is very sensitive to light while cinnamenylacetic acid is not.

II. Addition-Reactions of Diphenyltetramethylenebismethylenemalonic Acid.

1. With Hydrochloric Acid.—The acid combines very readily with 2 molecules of hydrochloric acid. When a solution of the acid in methyl alcohol was saturated with hydrochloric acid the insoluble methyl ester of an acid, formed by the addition of 2 molecules of hydrochloric acid, crystallized out. The substance was washed with alcohol and recrystallized from acetone.

0.1895 gram substance gave 0.4120 gram CO_2 and 0.1022 gram H_2O.

	Calculated for $C_{28}H_{30}Cl_2O_8$.	Found.
C	59.46	59.30
H	5.31	5.38

The ester is almost insoluble in methyl alcohol, ethyl alcohol, chloroform, and ether. It is readily soluble in boiling acetone, from which it separates, on cooling, in thick needles. It melts at 197° to 198° with evolution of hydrochloric acid.

The corresponding ethyl ester was made by saturating a solution of the acid in absolute alcohol with hydrochloric acid and allowing the liquid to stand for several days. It begins to separate after a few hours, but the amount of the product increases for several days. The ethyl ester is somewhat more soluble in boiling alcohol than the methyl ester and was purified by recrystallization from absolute alcohol.

0.2835 gram substance gave 0.6404 gram CO_2 and 0.1548 gram H_2O.

	Calculated for $C_{20}H_{24}Cl_2O_3$.	Found.
C	61.83	61.82
H	6.11	6.07

The ester crystallizes from acetone or absolute alcohol in long, slender needles. It is only very slightly soluble in ether, chloroform, methyl alcohol, and cold absolute alcohol. It is moderately soluble in boiling alcohol, readily soluble in acetone. It melts with decomposition at 185°.

2. Addition of Bromine.—The acid readily combines with 2 molecules of bromine, but the resulting addition-product is exceedingly unstable. It easily loses carbon dioxide and hydrobromic acid, and passes into a bromine substitution-product of an unsaturated dibasic acid, diphenyltetramethylene-bisbrommethyleneacetic acid.

Bromine was added, drop by drop, to 10 grams (1 molecule) of the substance suspended in glacial acetic acid until the color of bromine was permanent. The bromine disappeared rapidly until 7.5 grams (2 molecules) had been added. The acid dissolved as it was brominated. There was no evolution of carbon dioxide and the liquid contained only a small quantity of hydrobromic acid. The process was, therefore, one of direct addition. From the solution crushed ice precipitated a colorless product in clear, lustrous plates. These, however, rapidly changed into an impalpable white powder, while carbon dioxide was evolved and hydrobromic acid went into solution. The powder was filtered off, washed with water, dissolved in absolute alcohol, and reprecipitated by pouring the hot solution into twice its volume of hot water. It separated in colorless plates, which melted with decomposition at 245°. An analysis gave the following results:

0.1599 gram substance gave 0.3073 gram CO_2 and 0.0533 gram H_2O.

	Calculated for $C_{22}H_{18}Br_2O_4$.	Found.
C	52.17	52.36
H	3.56	3.70

The acid is insoluble in chloroform and ligroin, slightly soluble in ether and benzene, readily soluble in alcohol and acetone. In alkaline solution potassium permanganate oxidizes it rapidly and quantitatively to α-truxillic acid. This is doubtless the easiest way of preparing α-truxillic acid. For this purpose the crude product obtained by exposing cinnamylidenemalonic acid to the sunlight is filtered off, the moist solid suspended in its own weight of glacial acetic acid, and bromine added until the color is permanent. The solution is then poured into ten times its volume of boiling water and the precipitate removed by filtration as soon as the temperature of the water has fallen to 80°. After washing with cold water the precipitate is dissolved in a slight excess of a saturated solution of sodium carbonate. To the solution obtained in this way a saturated solution of potassium permanganate is added, at the ordinary temperature, until the color of the permanganate remains after vigorous shaking. The oxides of manganese are then dissolved by adding an excess of sodium bisulphite and acidifying with dilute sulphuric acid or, better, by passing a current of sulphur dioxide through the liquid. In either case the α-truxillic acid separates out in small, colorless grains, which melt above 270°, and after one crystallization from methyl alcohol, at 274°. The changes are represented by the following equations:

I. $C_6H_5CHCHCH{=}C(CO_2H)(CO_2H) + 2Br_2 =$

$HO_2C\,HO_2C\,C{=}HCCHCHC_6H_5$

$C_6H_5CHCHCHBrCBr(CO_2H)(CO_2H) \rightarrow$

$HO_2C\,HO_2C\,BrCBrHCCHCHC_6H_5$

$C_6H_5CHCHCBr{=}CHCO_2H + 2HBr + 2CO_2;$

$HO_2CHCBrCCHCHC_6H_5$

II. $$\begin{matrix} & C_6H_5CHCHCBr{=}CHCO_2H \\ & | \quad | \\ HO_2CHC{=}BrCCHCHC_6H_5 & \end{matrix} + 6CO + 2H_2O =$$

$$\begin{matrix} C_6H_5CHCHCO_2H & \\ | \quad | & \\ HO_2CCHCHC_6H_5 & \end{matrix} + 2HBr + 2 \begin{matrix} COOH \\ | \\ COOH \end{matrix}.$$

All of these reactions, beginning with cinnamylidenemalonic acid, are quantitative.

The methyl ester of diphenyltetramethylenebisbrommethyleneacetic acid was made by saturating a solution of the acid in methyl alcohol with hydrochloric acid and separating the product in the usual way. After recrystallization from alcohol the ester melted at 115°.

0.2050 gram substance gave 0.4043 gram CO_2 and 0.0780 gram H_2O.

	Calculated for $C_{24}H_{22}Br_2O_4$.	Found.
C	53.93	53.74
H	4.12	4.31

The ester is moderately soluble in methyl alcohol, readily soluble in ordinary alcohol and in acetone.

3. Addition of Acid Potassium Sulphite.—The acid combines with acid sulphites in the cold. A saturated solution of potassium sulphite was added to 5 grams of the acid until a clear solution resulted. After standing for eight hours an excess of dilute hydrochloric acid was added to the solution. An acid salt separated in fine, white needles. After one recrystallization from boiling water the air-dried salt was analyzed with the following results:

I. 0.1000 gram substance lost 0.0176 gram at 110°.
II. 0.1959 gram substance gave 0.0410 gram K_2SO_4.
III. 0.1639 gram substance gave 0.0349 gram K_2SO_4.

	Calculated for $C_{24}H_{22}O_{14}S_2K_2.6H_2O$.	Found. I.	II.	III.
H_2O	17.56	17.6	....	....
K	9.51	....	9.37	9.53

The salt is moderately soluble in cold water, readily soluble in boiling water, insoluble in alcohol. The corresponding neutral salt is very readily soluble in water.

III. Change of Diphenyltetramethylenebismethylenemalonic Acid into Cinnamylidenemalonic Acid.

As pointed out above, all the addition-reactions of the acid agree in composition and properties with the formula assigned to it, and it would be difficult to account for them by any other formula. The only fact that is not clearly accounted for by the formula is the surprising ease with which the acid can be changed back into cinnamylidenemalonic acid. The acid dissolves in cold concentrated sulphuric acid, and when the yellow solution is poured into ice-water pure cinnamylidenemalonic acid is precipitated. It is known that the tetramethylene ring is easily opened, and Liebermann[1] found that α-truxillic acid changes into cinnamic acid on distillation, but nothing that is known about tetramethylene compounds could lead to the expectation that the ring would be completely broken down by simple solution in cold sulphuric acid. The change seems to be connected with the peculiar character of the side chain since none of the other substances described in this paper is affected in the least by solution in concentrated sulphuric acid.

BRYN MAWR COLLEGE,
CHEMICAL LABORATORY,
July, 1902.

NOTE.

The Detection of Hydrocyanic Acid in the Presence of Sulphocyanic, Hydroferrocyanic, and Hydroferricyanic Acids and Their Salts.

Take about 25 to 50 cc. of the solution, from which the heavy metals and alkaline earths have been removed by boiling with sodium carbonate, add caustic potash and about 0.5 gram of pure aluminium filings. Let stand in a loosely stoppered flask about fifteen minutes. The potassium ferricyanide is reduced to ferrocyanide,

$$K_3Fe(CN)_6 + 4KOH + Al = K_4Fe(CN)_6 + Al(OK)_3 + H_2O + H_2.$$

Decant off a small portion of the clear solution, acidify, and add ferrous sulphate to test whether all the ferricyanide has been

[1] Ber. d. chem. Ges., **22**, 124.

reduced. If the reduction is complete, acidify the entire solution with hydrochloric acid, and precipitate the hydroferrocyanic acid with an excess of mercuric chloride solution.

$$H_4Fe(CN)_6 + HgCl_2 = Hg_2Fe(CN)_6 + 4HCl.$$

Shake well for a few minutes (do not heat), and then filter, repeating if necessary, until the filtrate is perfectly clear. Wash the precipitate with a little dilute mercuric chloride solution, and, if clear, add to the first filtrate. Now make alkaline with caustic potash, and filter off the mercuric oxide, wash, add to the filtrate a solution of ferrous sulphate and boil. The potassium cyanide is converted into potassium ferrocyanide :

$$FeSO_4 + 2KOH = Fe(OH)_2 + K_2SO_4;$$
$$Fe(OH)_2 + 2KCN = Fe(CN)_2 + 2KOH;$$
$$Fe(CN)_2 + 4KCN = K_4Fe(CN)_6.$$

Filter and wash, adding the wash-water to the filtrate. Acidify with hydrochloric acid and add ferric chloride solution. A dirt-colored solution is obtained. The iron sulphocyanate formed is decolorized by mercuric chloride, and the precipitate of Prussian blue can then be seen. If the solution is quite acid, and only a small quantity of hydrocyanic acid was present originally, the solution is green and no precipitate is formed until it has stood for a time. Keep all solutions cold.

LOUIS E. PREISS.

REVIEWS.

A TEXT-BOOK OF INORGANIC CHEMISTRY. By DR. A. F. HOLLEMAN, Professor Ordinarius in the University of Groningen, Netherlands. Rendered into English by HERMON C. COOPER, PH.D., Instructor in Syracuse University, with the co-operation of the author. First edition, first thousand. New York : John Wiley & Sons ; London : Chapman & Hall, Limited. 1902. pp. 458.

The German edition of this book has been so recently reviewed in this JOURNAL[1] that it only remains to call attention to the appearance of the American edition. Stress should be laid upon the fact that this book is not meant for beginners, and whoever places it in the hands of a student in the earlier stages of his work makes a fatal mistake. The reviewer's opinion of the book has already been expressed, and he wishes to congratulate Dr. Cooper upon the completion of the long and arduous task involved in bringing out the English edition of a work of this size.

H. C. J.

[1] This JOURNAL, **27**, 159 (1902).

THERMODYNAMIQUE ET CHIMIE. LEÇONS ÉLÉMENTAIRES A L'USAGE DES CHIMISTES. Par P. DUHEM, Correspondent de l'Institut de France. Professeur de Physique Théorique a L'Université de Bordeaux. Paris, Librarie scientifique A. Hermann. pp. 496. 1902.

The authority of Duhem in the field of thermodynamics, especially as applied to chemistry, is well recognized. His "Traité Élémentaire de Mécanique Chimique Fondée sur la Thermodynamique" has contributed much towards placing chemical mechanics upon an exact basis. The present work is far more elementary, avoiding the use of the higher mathematics.

Some of the more important subjects dealt with are work and force, quantity of heat and internal energy, chemical calorimetry, the principles of chemical statics, the phase rule, polyvariant systems, the displacement of equilibrium, bivariant systems—the indifferent point, mixed crystals, isomorphous mixtures, the critical conditions, chemical mechanics of perfect gases, chemical dynamics and explosives.

The work is written in that clear and concise style which is characteristic of the author, and is a valuable addition to the literature of chemical dynamics and equilibrium.

One statement in the preface seems to call for special comment. There are those who will differ from Duhem when he states that "nous n'avons voulu ni oublier, ni laisser oublier, que l'union de la Thermodynamique et de la Chimie s'etait accomplir en France, au laboratoire de l'immortel Henri Sainte-Claire Deville." While it is true that Deville carried out valuable experimental work in this field, it is also true that his theoretical deductions from his own work have been shown to be largely erroneous. In this connection the name of Horstmann should always be given the first place, since it was he who first successfully applied the mechanical theory of heat to chemical processes. H. C. J.

THE ELEMENTS OF PHYSICAL CHEMISTRY. By J. LIVINGSTON R. MORGAN, PH. D., Adjunct Professor of Physical Chemistry, Columbia University. Second edition, revised and enlarged; first thousand. New York: John Wiley & Sons; London: Chapman & Hall, Limited. pp. 344. 1902.

The appearance of the first edition of this book has already been noticed in this JOURNAL.[1] The author states in his preface to the second edition that "in preparing this edition I have endeavored to do three things: First, to bring the subject-matter itself up to date; second, to make, wherever possible, the relations clearer than before; and third, to make the book itself more useful to those studying the subject without an instructor. * * * Many things found superfluous

[1] This JOURNAL, 21, 459.

in the old edition have been omitted and a number of new relations added." H. C. J.

THE PRINCIPLES OF INORGANIC CHEMISTRY. By WILHELM OSTWALD. Translated with the author's sanction by ALEXANDER FINDLAY, M.A., B.Sc., PH.D. With 122 figures in the text. London: Macmillan & Co., Limited; New York: The Macmillan Co. 1902. pp. 785.

The German edition of this work has been reviewed in this JOURNAL.[1] It only remains to call attention to the appearance of the English edition of this important book. It is not too much to predict that this treatise on inorganic chemistry from the standpoint of physical chemistry, written by the master hand of Ostwald, will materially modify the teaching and study of this all-important branch of chemistry.

It is not at all clear to the reviewer why so little stress has been laid upon the Periodic System, since this generalization has certainly contributed much to the scientific study of inorganic chemistry.

The work of the translator, on the whole, is very well done. A few expressions which could have been improved upon have crept in, such as "Quantity Relations," and "with all the accuracy with which we can endow the measurement" on page 39; and "Other Methods of Preparation of Hydrogen" on page 83. When, however, we consider the large amount of drudgery which is involved in translating a work of this size, we heartily congratulate the translator upon the successful completion of his task. H. C. J.

INTRODUCTION A L'ÉTUDE DE METAUX, LEÇONS PROFESSÉES A LA FACULTÉ DES SCIENCES. Par ALFRED DITTE, Professeur de Chemie a l'Université de Paris. Paris: Société d'Éditions Scientifiques. 1902. pp. ii + 488.

In looking over this volume one is very strongly reminded of Wurtz's famous phrase: "La Chemie est une Science Francaise." This statement is not very far from the truth in the particular field which the book covers, particularly of that portion of it treating of the properties of metals, and it is not surprising to see the names of so many French investigators in this subject. The subject has been attractive in itself, and the study of the properties of metals and alloys has been fostered by the Society for the Encouragement of National Industry. Under this influence the knowledge of the properties of metals has been greatly extended, notably by the beautiful researches of Osmond, Le Chatelier, Charpy, and others.

The subject is presented in a manner essentially different from the way it would be presented in any other language.

[1] This JOURNAL, **25**, 83.

The tendency of the present day to specialize is so great that it is somewhat surprising to see a book attempting to cover so wide a field. The author begins with the minerals as they come from the earth and traces the history of the changes which a metal may be subjected to until it again returns to the earth. Surely, a very wide field.

As far as the reviewer is able to judge such an extensive subject, the ground is well covered, except that the author has suffered from a certain amount of provincialism which has allowed him in many cases to accept the French workers as authority and to allow the important work of others to pass unmentioned. It might perhaps be better to say that the author has so selected his subjects as to confine himself largely to the French investigators, but the whole book would have been more valuable if the researches of foreign workers had been given greater consideration. As it is the book contains perhaps a greater number of interesting facts in regard to the properties of metals, exclusive of books devoted to iron and steel, from the purely scientific point of view than any other one volume.

The book is divided into two parts: I. The metals considered among themselves; II. the metals in their relations to other substances. In the first part is considered the natural occurrence and origin of minerals, the preparation of artificial minerals which has been investigated almost solely by the French, the concentration of ores and the various metallurgical processes, and of the properties of the metals themselves there is discussed the isomeric modification of metals, and the more general properties such as fusibility, conductivity for heat and electricity, magnetism, tenacity, ductility, etc., and the causes which modify these properties.

In the second part the author treats of the properties of alloys and the study of their constitution by means of the microscope, their fusibility and electrical conductivity curves, and the more general properties of various alloys of iron, nickel, copper, etc. The action of various elementary gases and other elements, acids, bases, and salts, with special emphasis on the thermo-chemistry of the reactions are described; also the effect of atmospheric agencies on metals and alloys, and, finally, the various classifications of the elements into natural systems.

The book is very attractively issued, but its value would have been greatly increased had it been provided with a more serviceable index.

HENRY FAY.